ENVIRONMENTAL CONTAMINANTS IN PETROLEUM REFINERY WASTEWATERS:

AN ASSESSMENT OF CURRENT INFORMATION AND A MONITORING APPROACH

MUNICIPAL-INDUSTRIAL STRATEGY FOR ABATEMENT JOINT TECHNICAL COMMITTEE

-ONTARIO MINISTRY OF THE ENVIRONMENT
-ENVIRONMENT CANADA
-ONTARIO PETROLEUM ASSOCIATION

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ENVIRONMENTAL CONTAMINANTS

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AND A MONITORING APPROACH

A Study Prepared for:
The Joint Industry/Government Technical Committee,
Petroleum Refining Sector,
of the
Municipal Industrial Strategy for
Abatement Program

By the Trace Contaminants Working Group

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1.0 EXECUTIVE SUMMARY

This report summarizes the findings of an Industry-Government Trace Contaminants Working Group that was assigned the task of reviewing the existing information on trace contaminants in treated oil refinery wastewaters. This review, and the development, by the MOE of a Monitoring and Reporting Regulation specifically for the petroleum industry proceeded simultaneously.

The working group reported to the full MISA (Municipal-Industrial Strategy for Abatement) MOE/Environment Canada (EC)/OPA Technical Committee, which was organized to provide technical advice to the Environment Minister of Ontario. This full MISA technical committee was assigned the task of reviewing a conceptual draft of the MOE monitoring and Reporting Regulation and required the findings of this present report as a basis for their review.

The working group concluded that the present database is reasonably complete and with a few exceptions, sufficient for the development of monitoring requirements. Some additional work was recommended prior to finalizing the Monitoring and Reporting regulations and a study was completed in the Fall of 1986 by the Petroleum Association for Conservation of the Canadian Environment (PACE) with a report now available.

The available evidence indicates that under good operating conditions the treated effluent from Ontario petroleum refineries contain only a few trace contaminants, and their concentrations are consistently less than 50 parts per billion.* Such levels reflect over 99.9% removal of the contaminants entering the treatment system. Studies of treated effluent from other petroleum refineries in Canada and the United States confirm this finding. These results are expected from an understanding of what a petroleum refinery does, what wastewaters are generated and

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*Note: 1 part per billion is 1 second in 31 years, 259 days, 1 hour and 46.7 minutes.

how various wastewater treatment systems (within the process area and external) function.

The purpose of the Monitoring and Reporting Regulation is to provide a data base for the eventual setting of contaminant control limits. It is important that this information be collected on a uniform and consistent basis for each industrial sector.

The Working Group agreed that good science required the monitoring of treated but undiluted wastewaters to establish a meaningful trace contaminants data base.

The Working Group in their review and discussions addressed a Conceptual Monitoring and Reporting Regulation developed by MOE. This conceptual MOE regulation has four contaminants monitoring lists, each of which has a different sampling frequency and purpose. The four pollutant lists are:

1. Characterization

   The Ontario Effluent Priority Pollutants List, which includes numerous compounds not expected in treated petroleum refinery effluents, is the basis for periodic characterization. All industrial sectors will use MOE's Effluent Monitoring Priority Pollutants List (EMPPL). The reported results will be accompanied by a detailed interpretive report. The Ontario EMPPL includes more compounds than the U.S. EPA Priority List while also excluding some U.S. EPA Priority Pollutants.

   The Working Group recommends that wastewater characterization include a series of studies starting with an initial characterization study followed by additional studies as required (see section 6.0).

   In Canada, the petroleum industry has provided characterization data specific to this industry through PACE studies. However, the list of contaminants studied by PACE has varied and has not included all contaminants on the Ontario EMPPL. The stepwise PACE

studies answered information gaps that arose from each previous study to provide a reasonably comprehensive understanding of treated wastewater quality. The PACE study in the fall of 1986 of two Ontario Refineries (19) continues this approach. Although there are a few information gaps, these and other studies can be used to predict the trace contaminant quality of effluent for well operated effluent treatment systems, especially for contaminants of interest to the Joint Technical Committee such as Benzene/Toluene/Xylene (BTX), Polynuclear Aromatic Hydrocarbons (PAHs) and metals.

2. Pollutants Monitored Daily (Control)

The conceptual MOE monitoring regulation requires that a number of pollutants be monitored on a daily basis to demonstrate that the effluent treatment system is being operated consistently.

Other parameters such as dissolved oxygen, the dissolved oxygen uptake rate, MLSS, SVI, aeration basin pH, etc., are used to control the treatment system. It is recommended that for control of petroleum effluent treatment systems, the pollutants Total Suspended Solids (TSS), Phenolics (4AAP), pH and perhaps Total Organic Carbon (TOC) be monitored daily. Industry is already doing this on a daily basis and the data show that well operated treatment systems discharge low levels of these pollutants.

3. Pollutants Monitored on a Three Times Per Week Basis

The conceptual MOE monitoring regulation requires the monitoring of ammonia-nitrogen, organic carbon, oil and grease, sulphides, volatile aromatics (benzene, toluene, xylenes, ethylbenzene), zinc and chromium on a frequency of three times per week.

Although well operated effluent treatment systems are expected to discharge such contaminants only occasionally and in the parts-per-billion concentration range, some specific compounds should be monitored to confirm the effectiveness of removal. The Working Group agreed that the following parameters should be monitored on a frequency of more than monthly but less than daily:

- volatiles (benzene, toluene, xylenes, ethylbenzene: indicator priority pollutants)
- oil and grease
- ammonia-nitrogen.

Where a refinery uses either zinc, chromium or phosphorus, these should be frequently monitored by the refinery.

4. Monthly Pollutant List

The conceptual MOE monitoring regulation requires the monitoring of 12 effluents per year for a comprehensive list of parameters including aromatic hydrocarbons, chlorinated volatiles, acids, a number of metals, cyanide and additional conventional parameters. The Working Group did NOT agree as to which of two concepts should be used to develop a Monthly Demonstration List, nor with the necessity of a fourth list. The Petroleum Refineries had provided information on pollutants entering and leaving the effluent treatment system. One concept was to use the existing data base on the treated effluent from the biotreater. The other concept was to use the data from the Intermediate Treatment Wastewaters, (e.g. the feed to the biotreater). The Working Group agreed that the biological portion of the effluent treatment system was critical to removing trace organic contaminants.

The Working Group agreed that a compound listing and delisting mechanism should be written into a Monitoring Regulation. This mechanism should consider frequency of parameter detection, toxicological information, environmental persistence, analytical accuracy at low levels and best available technology for removal. The listing/delisting mechanism would require additional resources and time for development.

The Working Group also agreed that MOE should provide to the public, within 4 weeks of receipt, a proper evaluation of the analytical results. It is well recognized that unless analytical data are explained, they can actually be misleading. An explanation must always accompany parts per billion analyses.

2.0 INTRODUCTION

In June 1986, the Ontario Government published a policy and program statement on controlling municipal and industrial discharges into surface waters. The Government's White Paper was entitled "Municipal-Industrial Strategy for Abatement (MISA)."

The Government's intent is to develop comprehensive wastewater based regulations that will cover all major industrial and municipal discharges to the environment. Monitoring regulations will first be developed, requiring each company or municipal plant to monitor its effluent for a wide range of contaminants. This will be followed by abatement regulations which will establish best available technology (BAT) standards for each sector, and will require each discharge to meet specific standards. Ontario's petroleum refineries already have in place best available effluent treatment technology as defined by United States Environmental Protection Agency (U.S. EPA). However, all refineries do not have the same degree of treatment. The standards will be based on total loading of individual contaminants rather than contaminant concentrations.

In dealing with the total industrial base, a sectoral approach has been taken. The June 1986 MISA document lists eight industrial sectors to be separately regulated. Monitoring regulations are to be developed for each sector. To provide the best review possible of pertinent scientific knowledge, the Ontario government has convened a Technical committee for the PETROLEUM REFINING industry. This committee of knowledgeable scientists from government and industry assigned to a working group of four the task of reviewing existing knowledge about petroleum refining and the wastewaters generated by this activity. A Ministry of Environment (MOE) conceptual Monitoring and Reporting Regulation was also reviewed and compared with findings of the present review.

2.1 Objectives

The working group objectives were:

- to review and organize existing data on refinery wastewaters and to present this information in an understandable form.

- to make specific comments regarding the adequacy of the existing trace contaminants data for characterizing and understanding treated effluent quality.

- to consider the scientific implications of the conceptual Monitoring and Reporting Regulation with respect to a proper assessment of petroleum effluent quality consistent with the intent of MISA.

2.2 Approach

To meet the above objectives, the working group followed well established principles in their scientific review of the present information base. It was necessary to review:

- the nature of crude oil processed by a petroleum refinery, the processes utilized to make the various marketable end products and the use of water in the processes (see Section 3.0 and Appendix A).

- the sources and general characteristics of refinery wastewaters and how these wastewaters are treated prior to discharge (see Section 4 and Appendix B).

- the considerable volume of data generated by numerous studies that have addressed the issue of contaminants in petroleum wastewaters. These studies have been carried out in Canada and the United States (see Section 5).

This Working Group of four consisted of:

Walter Suboch, Ontario Ministry of the Environment (MOE)
Gerry Rees, Ontario Ministry of the Environment (MOE)
Allan Maynard, ASL Laboratories, Vancouver, B.C. - a consultant to the Ontario Petroleum Association (OPA)
Jim Greenshields, Suncor in Sarnia - on behalf of OPA

This Working Group presented this report to the full MISA MOE/Environment Canada/OPA Technical Committee. This committee is to provide technical advice to the Minister of Ontario's Ministry of the Environment on the effluent from petroleum refineries.

3.0 PETROLEUM REFINING

To understand the quality and quantity of wastewater generated in petroleum refining, one must consider the feedstock (crude oil), the various processes and the usage of water. A petroleum refinery operates 24 hours a day and seven days a week with infrequent shutdowns every one to two years for major maintenance.

Petroleum refineries process a naturally found resource, crude oil, into a variety of end products including:

- motor gasoline (used in cars, trucks, boats and aircraft)
- heating and industrial fuel oils (kerosene, stove oil, diesel fuel, bunker)
- lubricating oils
- petrochemical feedstocks
- asphalts

A typical Western Canadian crude oil consists of 25% gasolines, 15% distillates, 12% bunker and 38% other hydrocarbons. This 38% is cracked to form gases, gasolines, distillates and bunker. The original 25% gasoline needs processing to be acceptable motor fuel. The refining process can increase the gasoline yield to 55% and distillate to 20% while using 8% for fuel. The aromatics - benzene, toluene and xylenes - are not only key components of unleaded gasolines and also intermediate petrochemical feedstocks for the organic chemical industry, but tend to be the trace contaminants found in treated effluent.

3.1 Crude Oil

Crude oil is primarily a mixture of hydrocarbons which are molecules that consist of hydrogen and carbon atoms. The major classes of compounds are:

- paraffins - straight chain saturated hydrocarbons
- olefins - unsaturated hydrocarbons (usually low in crude oil but quantities increased by subsequent processing)
- naphthenes - ringed components, some of which are aromatic such as benzene and toluene.

Over 3000 compounds have been identified in crude oil but almost all fit into the above categories. The paraffins (n - and isoalkanes) by far comprise the major components of crude oil (1,2). The naphthenes are less predominant but are of more significance environmentally. In the boiling range of gasolines, naphthenes are usually converted by processing into aromatic compounds. In operating a refinery to yield maximum gasoline, the objective is to produce the most aromatic hydrocarbons. The polycyclic hydrocarbons which boil at above 625°F are cracked to lower their molecular weight. Temperature sometimes with a catalyst is used to break larger molecules into smaller molecules or pieces.

Crude oils also contain, along with the hydrocarbons, sulphur (0.5 to 3.0%) and nitrogen (0.5 to 3.0%), some heavy metals (in the ppm range) and inorganic salts such as sodium chloride, etc. (1). A desalter is used to remove chloride salts before crude oil is processed. These salts are corrosive to steel.

3.2 Processes

The petroleum refinery is a continuous operation. The crude oil distillation unit makes the primary separation with the resulting "cuts" becoming the feed for secondary and tertiary processes. The various processes produce specific hydrocarbons which may be found at trace levels in the wastewaters.

The typical Ontario Petroleum Refinery separates and rearranges hydrocarbon molecules to produce motor gasolines (primarily in spring and summer) and heating fuels (primarily in fall and winter). Although many different process units are used to convert crude oil into specific products, the processes themselves can be broken down into the following categories:

- separation - usually by distillation into different boiling range components or "cuts" (gasoline boils from 90°F to 350°F, stove oil from 350° to 400°, etc.).

- conversion - used to change the size or shape of the hydrocarbons to those of higher economic value. Typical examples are Catalytic Crackers, Cokers and Thermal Crackers (which break down large hydrocarbons into smaller ones), Catalytic Reformers and Isomerization Units (which reshape the molecular structure) and Alkylation or Polymerization Units (which join two or more hydrocarbon molecules together).

- solvent extraction of the aromatics (benzene, toluene, xylene) from reformate produced at the catalytic reformer.

- steam or pyrolysis cracking to produce olefins like ethylene which are used to make synthetic organic compounds.

- lubricating oil processing which may include hydrogen treating or phenol treating.

- blending - mixing of two or more products.

- catalytic removal of the organic sulphur and nitrogen compounds (hydrogen is added to make these into gaseous compounds which are distilled or stripped out - wastewater sources).

- washing or scrubbing of gases or liquids by caustic soda or amine treatment to remove hydrogen sulphide, mercaptans, phenols, cresols and naphthenic acids. Some patented processes use caustic, catalyst and air to convert sulphides to disulphides.

It is important to note that petroleum refining is distinct from chemical manufacturing in that new compounds, unrelated to the raw materials, are not formed. Synthetic organic compounds are not made. Hydrocarbons are either broken down into smaller hydrocarbons or their structures are slightly reorganized - simply to enhance their properties for end use. CHLORINE OR OTHER HALOGENS ARE NOT USED TO MAKE ANY END PRODUCTS. Chlorine however, can be used to control algae growth in once-through cooling water.

One might find halogenated compounds in cooling water that has been treated by chlorine though likely at very low concentrations. It is emphasized that the similarity of chemical processes on similar raw material is consistent with similar end-products and of course comparable effluent quality. Thus, the raw effluent from Ontario refineries should be of comparable but not necessarily identical quality to other petroleum refineries in other parts of Canada and the United States.

A more detailed discussion of crude oil and the refinery process is presented in Appendix A. This Appendix also contains a summary of the refining processes used by each Ontario refinery. Note the core of similar processes.

3.3 Wastewater Sources

Before primary distillation, all crude oils must first pass through a desalter which removes salts such as sodium chloride from the crude oil, as inorganic salts must be kept out of petroleum products.

Since distillation or separation by heat is the dominant refining process, the separation products must be cooled by indirect contact with a cooling medium - water. Thus, over 90% of the water is used in a refinery as a heat transfer medium. The potential exists for leaks into cooling water, and leaks have occurred in Ontario.

Almost all petroleum products are sold as water-free or "dry". After a product has been stored for several days in a tank, water will settle to the bottom. This water can be drawn off and treated.

Newer refinery designs recirculate large amounts of water through cooling towers with any contaminated cooling water being treated and reused. Although fresh water make-up to these systems is required, only a very small amount of cooling tower "blowdown" is discharged into the refinery system. About 90% of the make-up water is evaporated at the cooling towers.

Refinery process wastewater is formed from a variety of processes:

- desalters (inorganic salts)
- crude distillation units (condensed steam from the side-cut strippers)
- fluid catalytic crackers (steam to fluidize catalyst plus side-cut strippers)
- hydrocrackers (sour wash water to prevent fouling of exchangers)
- various thermal crackers (sour quench water)
- gas recovery units (small amount of sour waters)
- alkylation units (wastewaters contain traces of acid)
- solvent extraction units (normally no wastewaters)
- hydro desulphurization units (sour wastewaters)
- asphalt oxidation (quench waters contain phenolics)
- cooling water blowdown (inorganics from incoming water and possible treatment chemicals)
- boilerhouse blowdown (inorganics from incoming water)
- steam (ethylene) cracker (sour phenolic wastewaters)
- sulphur recovery (normally no wastewaters).

Sour waters are highly odourous due to the hydrogen sulphide, ammonia and phenolics in them.

There is also wastewater from sources other than the above 14 from process units:

- ships - ballast water
- tank farm drainage
- rain water runoff from roads, parking lots
- brines from treating fresh intake water
- sanitary waste
- leachate or surface runoff from sludge landfarm areas

Newer petroleum refineries do not use once-through cooling water. Instead, cooling is done by a combination of air coolers and recycled water. This is done at the Texaco (Nanticoke), Petrosar (Corunna now part of Polysar) and Petro-Canada (formerly BP at

Oakville) refineries. Some individual unit processes have their own cooling towers - ESSO Petroleum (Sarnia), Shell (Corunna), Petro-Canada (formerly Gulf at Clarkson).

The following summary shows the difference in water usage. Smaller effluent volumes can be treated for longer times without being cost prohibitive.

Refinery	Water Usage Cubic Metres/Day	Nominal Capacity Barrels/Stream Day
Esso Petroleum at Sarnia	215,700 (18,000)*	120,000
Petro-Canada at Clarkson	260,000 (13,200)*	60,000
Petro-Canada at Oakville	4,800	82,000
Petrosar Limited at Corunna (part of Polysar Limited)	6,580	100,000 (originally 170,000)
Shell Canada at Sarnia	234,700	85,000
Suncor at Sarnia	119,000 (15,000)*	85,000
Texaco Canada at Nanticoke	6,810	110,000

*process wastewaters only

4.0 WASTEWATER TREATMENT

All Ontario refineries have sour water strippers. The stripper usually removes 95 - 99% of the hydrogen sulphide, 80 - 95% of the ammonia and 20 - 30% of the phenols (3,4). The resulting gas is sent to a unit for conversion into by-product sulphur. The stripped sour waters are often used in the crude oil desalter where a good part of the phenols are absorbed in the crude oil.

The wastewaters from the various units are collected and diverted to the wastewater treatment facility. The following summary indicates the typical ranges of conventional parameters untreated (before the biotreater) and treated wastewaters from two well operated Ontario petroleum refineries:

	Before Biotreater*	After Biotreater*
Dissolved organic carbon, milligram/litre	15.7 - 51.6	8.8 - 20.1
Suspended solids, milligram/litre	24 - 70	3 - 80
Oil & grease, milligram/litre	6.5 - 46.9	5.1 - 29.2
Total phenolics, milligram/litre	0.105 - 28.5	0.004 - 0.084
Ammonia nitrogen, milligram/litre	<1. - 25	<0.01 - 20.3

Specific trace contaminants are also found and this information is found in Section 5.

* from the most current PACE Ontario Refinery Study (19)

All Ontario refineries treat effluent in a similar manner involving primary (oil removal) and secondary (biological oxidation) treatment. These treatment methods are discussed in more detail in Appendix B, but involve the following basic steps:

- primary oil removal (API Separator) - removes the majority of oil by skimming for recycle to the crude unit.

- secondary oil removal (Dissolved Air Flotation - (DAF) or Dual Media Filtration) - removes more dispersed oil by air flotation for recycle.

- some refineries have a separate neutralization and equalization stage prior to the biological treatment plant.

- biological oxidation - organic materials are biologically oxidized (secondary treatment); micro-organisms convert hydrocarbons to carbon dioxide and water.

- clarification - to remove biomass.

THE ABOVE FOUR SEQUENTIAL PROCESSES OF WASTEWATER TREATMENT HAVE BEEN DEFINED BY THE ENVIRONMENTAL PROTECTION AGENCY (EPA) AS BEST PRACTICABLE TECHNOLOGY (BPT) (3). EPA HAS SET BEST AVAILABLE TECHNOLOGY (BAT) LIMITS AS EQUAL TO BPT EXCEPT FOR PHENOLICS AND CHROMIUM FOR WHICH BAT IS MORE STRINGENT. Appendix B has a schematic for each Ontario refinery describing flow measurement, sampling, analyses and the effluent treatment system.

All Ontario petroleum refineries can treat stormwater and/or ballast water in the biological treatment part of the effluent treatment system. The first few hours of a rainstorm flushes various areas of a refinery clean of hydrocarbons. This portion of stormwater is usually treated biologically.

Flow through the effluent treatment system is carefully controlled. Overloading the system hydraulically reduces effectiveness of pollutant removal. Also, a sudden shock will upset the biological balance and performance will drop. The shock can be either an increase in pollutants or an influx of unusual pollutants.

The performance of the various effluent stages was described by a Petroleum Association for the Conservation of the Canadian Environment (PACE) (literature review and other information) report on the removal of trace contaminants by API separators, air flotation units and biological treatment units for the removal of trace organic contaminants (6). This study found trace contaminants reduction occurred as follows:

API Separator	• most organic compounds associate preferentially with the oil phases and are thus removed with the skimmed oil
Air Flotation	• again organics removal with the oil phase as with API but a different residual oil drop size • removal by volatilization
Biological Treatment	• biological oxidation or conversion to carbon dioxide and water • enmeshment in or absorption on the biological floc (sludge) • volatilization from aeration.

Similar findings were reported by Oklahoma State University (7).

A field and laboratory study was carried out by PACE (8) to actually assess the fate and transformation of priority pollutants in the biological treatment system. It was demonstrated that overall removal at the refinery studied was greater than 99% with most of the contaminants removed by oil skimming at the API unit (and therefore recycled back to the process units). Of the compounds entering the biological unit, greater than 99% were removed by biological degradation. Volatilization and sludge adsorption and/or enmeshment were not found to be the major means of removal in the biotreatment portion of the effluent system studied.

An International Joint Commission Great Lakes Task Force reviewed the progress made by the Petroleum Refining Industry to reduce its pollutants discharges and concluded that "A significant improvement in the quality of wastewater being discharged from Canadian and United States refineries has been observed since 1976. This improvement has occurred both on a basis of total load and on a basis of loading per unit of crude oil processed, and is a result of efforts by the industry to meet the applicable requirements imposed by the jurisdictions. This improvement has been primarily achieved by upgrading treatment facilities, and by improved water management" (18). There are other IJC Task Force recommendations such as operator training to manage the effluent treatment system. PACE has held two operators workshops to transfer treatment technology. Ontario refineries train and rotate most operators to make them not only competent operators but to appreciate the environmental significance of the effluents being treated.

5.0 PRESENT DATA BASE CONCERNING CONTAMINANTS IN REFINERY WASTEWATERS

As a result of the trend towards environmental contaminants legislation, the refinery industry in the United States and Canada, starting in the late 1970's, undertook a series of studies concerning contaminants in refinery wastewaters. On both sides of the border, these studies were funded jointly by industrial associations (American Petroleum Institute [API] in the U.S. and Petroleum Association for the Conservation of the Canadian Environment (PACE) in Canada) and by the Federal Governments (EPA in the U.S. and Environment Canada [EPS] in Canada). The joint industrial association plus government approach to this type of research is very beneficial because of the sharing of high cost and resource requirements.

Refinery wastewaters are well suited to this approach because they are relatively uniform from one plant to another in that:

- raw materials are very similar (in Ontario, the feedstock or crudes are produced in the Western Canadian oil fields of Alberta, British Columbia and Saskatchewan)

- the process units are similar (Appendix A)

- most refineries use similar wastewater treatment procedures as outlined in Section 4.0.

As such, it was postulated and later demonstrated that properly designed sequential studies at a few refineries are appropriate to generally characterize refinery wastewaters from all or most refineries. Of course, site specificity must be addressed as some individual refineries may have unique problems such as incoming river water contaminated with chlorinated hydrocarbons. While petroleum refineries have many similarities, they are not identical regarding process units, process unit combinations, wastewater treatment systems, etc.

The presentation below summarizes the studies carried out by PACE and EPS in Canada (Section 5.1), the API and EPA in the U.S. (Section 5.2), and work by individual refineries to examine site specificity (Section 5.4). It also presents the findings of a recent joint Government study (Environment Canada - MOE) concerning discharges to the St. Clair River (Section 5.3).

5.1 Pace Studies

In Canada, the largest data base pertaining to characterization of refinery wastewaters has been produced in studies jointly funded by PACE and Environment Canada. Four field/laboratory studies plus three reviews were completed between 1980 and 1984, some of which have only recently been published. The following five projects represent a logical study sequence to understand true contaminants in petroleum refinery effluents. All sampling was done by consultants; no refinery personnel were involved.

1979/1980 - Survey of Trace Substances in Canadian Petroleum Industry Effluents (9)

On the basis of findings in a preliminary study carried out by the American Petroleum Institute (API) and in consideration of parameters included in Canadian legislation, a list of 58 contaminants (organic and inorganic) was defined for study. The project involved analysis of plant intake waters, biological treatment influents and final plant effluents collected from six oil refineries (3 were Ontario refineries) and a tar sands upgrading plant. A total of forty-six samples were analyzed for the 58 specific parameters plus additional inorganic and organic materials that were identified during the analysis procedures.

1980/1981 - Characterization of Organic Substances in Canadian Oil Refining Industry Effluents (10)

The second study was designed to provide a more complete characterization of refinery wastewaters with respect to trace organic substances. Three refineries, one from Ontario, were studied. This work was undertaken as a result of the recommendations of the first study (9) in which many compounds other than those on specific contaminant list, were routinely detected in refinery wastewaters (e.g. alkyl substituted phenols, alkyl-benzenes and polynuclear aromatic hydrocarbons).

1981/1982 - Evaluation of the Variability of Trace Organic Substances in Petroleum Refinery Effluent (11)

The samples analyzed during the previous two studies (9, 10) were twelve or twenty-four hour composite samples collected from a number of Canadian refineries. Therefore, the variability of effluent quality over time (in terms of trace substances) could not be addressed. A long term study was undertaken involving the analysis of fifteen intake waters and fifteen effluents collected from a Sarnia refinery over a two month period. The 24 hour composite samples collected were analyzed for a modified list of parameters derived from the findings of the previous studies. A rigorous quality assurance program was incorporated into this study which allowed an evaluation of analytical variability and its comparison with effluent variability.

1982/1984 - Fate and Transformation of Selected Trace Organics in Refinery Wastewater Treatment (8)

One of the most significant conclusions in each of the three previous studies was that the current treatment technology at Canadian refineries is successful in removing many trace organic compounds from untreated wastewaters. However, no information was

obtained on the fate of these compounds within the treatment system. To assess this, a project was undertaken which involved sampling and analysis of raw wastewaters entering the treatment process, final effluent, return and disposal sludges plus air leaving the treatment units.

Three review documents were also prepared (6, 12, 13) to assist in the overall interpretation of the results obtained in the field/laboratory studies. Finally, a summary report was prepared which discussed the results of all the above studies (14). This summary report is an important precursor to the present report in that it outlines the historical background in terms of contaminants legislation and the purpose of the PACE studies.

5.1.1 Analytical Methodology

State of the art analysis methods, based on EPA publications, were used throughout the PACE projects. While basically the same methods will be required under the proposed MISA regulations, methods have improved between 1979 and 1986. Summaries of these methods are presented in Appendix C.

Comprehensive quality assurance programs were carried out with all the projects which provided a detailed evaluation of the EPA methodology for priority pollutant analysis. It was concluded that the random error of the EPA methods could be sufficiently large to preclude the use of individual measurements as indicators of organic priority pollutant concentrations in refinery effluents. Analytical variability as high as 50 to 100% of the reported results, has been presented in the literature (11, 15). Methods also include sampling, storage, sample preservation, sample extraction and analysis. The analytical instrument measurement is the most precise step. Variability is introduced in all steps. Mean and median concentrations provided a more accurate representation. This should not be used as a criticism of the EPA methodology or invalidate the results of any research. It must be remembered that the methodology was developed to concurrently measure at least 87 organic compounds.

Better results (i.e. more accurate and more precise) are attainable by analyzing for compounds or groups of compounds on an individual basis. In this manner, extraction methods and detection methods can be used that are optimized for the chemical characteristics of the specific compounds under review. This approach, however, would be very time consuming and not cost effective for full survey programs such as those described above.

The precision and accuracy problems of the EPA methodology does not alter the overall interpretation of the results obtained for the PACE studies, especially in consideration of the amount of the data obtained. Individual results may occasionally be in error but the mean results truly reflect refinery effluent quality with respect to concentration of trace organic compounds.

5.1.2 Substances Detected and Not Detected in Refinery Wastewaters

The analytical work produced a large volume of data and a great deal of effort was directed towards summarizing this data into manageable formats. Most of the analytical work was for determination of contaminants on the 1976 EPA priority pollutant list. Table 1 provides a summary of priority pollutants detected and not detected in refinery wastewaters.

Eighty percent of the priority pollutants were either not detected (see category 1 in Table 1) or only rarely detected (see category 2 in Table 1) in refinery wastewater. The contaminants that were rarely detected were not considered to be associated with the oil refining process. Certain compounds were present because of their occurrence in the raw feed water (intake water). PCBs and hexachlorobenzene were found at very low concentrations (well below 1 ppb) in both untreated and treated wastewaters.

TABLE 1: PRIORITY POLLUTANTS DETECTED AND NOT DETECTED IN TREATED REFINERY WASTEWATERS (PACE STUDIES 1981-1984)

Category	Contaminant or Contaminant Class	Concentration in Effluent (µg/L) Min.	Max.	Median*[3]
1. Contaminants not detected	- most of the Volatile Halogenated Compounds - Polychlorinated Terphenyls - Polybrominated Biphenyls - Chlorophenols and Nitrophenols - Nitrosamines - Haloethers - Beryllium, Silver, Thallium			
2. Contaminants rarely detected in ITW or effluents	- Polychlorinated Biphenyls (PCB) - Hexachlorobenzene - Some Volatile Halogenated Compounds - Mercury & Selenium			
3. Contaminants frequently*[2] in ITW and occasionally*[2] in final effluents	- Phthalate Esters	ND	157	ND/1.
	- Polynuclear Aromatic Hydrocarbons	ND	13	1./ND
	- Metals (antimony, arsenic, cadmium, lead, nickel)	ND	38	-
	- cyanide	ND	140	ND/-
4. Contaminants detected at high concentrations in ITW and consistently or frequently detected in final effluents	- Benzene	ND	770[4]	1./7
	- Toluene	ND	840*[4]	2./1.
	- Ethylbenzene	ND	23	1/ND
	- Naphthalene	ND	59	1/1
	- Phenol	ND	900*[4]	ND/1
	- Zinc	8	240	38/-
	- Chromium	2	700	9/4
	- Copper	3	37	7/-

Note: Some compound or classes of compounds may be shifted from category 3 to 4 or vice versa.

ITW = Intermediate Treatment Waters ND = Not Detected

* [1]Frequently defined as generally more than 50% frequency of dection; the 50% is arbitrary, 30% or other % occurrence could be used.
* [2]Occasionally defined as generally less than 50% frequency of detection; the % used is arbitrary.
* [3]Median calculated from two studies - the seven refinery study (9)/ and the variability study (11). They were only determined for compounds or compound groups in category 3 & 4.
* [4]The maximum values of these parameters were abnormally high due to one West Coast Refinery that did not have a successful biox unit.
Note: false positive analytical errors may be identified in previous studies using the most current knowledge about the analytical limits of detection.

The detected compounds were categorized into two groups (category 3 & 4) as shown in Table 1; those that were detected at a frequency of less than 50% in final effluents (category 3) and those detected at a frequency of more than 50% in effluents (category 4). It was recommended in the PACE summary report (13) that category 4 compounds be used as a means of monitoring refinery effluents with respect to trace contaminants.

The analysis methods also allowed an identification of other organic compounds that were not on the original target contaminant lists. In the initial two studies (8, 9), additional mass spectrometry work was carried out to identify as many compounds as possible. In the two later studies, some of these "non-priority pollutants" were added to the target lists and therefore quantitated. The additional substances found in refinery wastewaters are summarized as follows:

Consistently detected in effluents	- Aliphatic hydrocarbons
Frequently*[1] detected in effluents at low ppb*[2] concentrations	- Alkyl-benzenes - Alkyl-napthalenes - Alkyl-phenols
Occasionally*$_3$ detected in effluents at low ppb concentrations	- Alkyl polynuclear aromatic hydrocarbons - Mercaptans - Thiophenes - Ketones - Acetone - Fatty Acids

*[1] defined as more than 50% frequency of detection

*[2] low ppb defined as approximately 0-50 ppb

*$_3$ defined as less than 50% frequency of detection

5.1.3 Major Conclusions of PACE Studies

The following conclusions were made in the 1985 summary report by Maynard (14), (only the most significant of which are noted below):

- "present treatment systems in use at most Canadian refineries are capable of reducing and in some cases eliminating trace organic and trace mineral substances from refinery wastewaters."

- "most of the contaminants on the EPA priority and Canadian hazardous pollutants lists were not present in refinery wastewaters (i.e. 80% of the contaminants on the EPA list were not routinely detected in refinery effluents)."

- "conventional parameters such as oil and grease, total organic carbon, suspended solids and total phenols provide a good indication concerning the effectiveness of refinery wastewater treatment."

- "some parameters were detected and considered to characterize refinery wastewaters with respect to contaminant concentrations (see Category 4 in Table 1)."

- "variability of refinery effluent at the one refinery studied was not considered problematic. A major contributor to the variability of results was analytical variability."

- "specific conventional parameters are not reliable surrogates for trace organics concentrations although they will provide a perspective on the general effluent quality."

Note: It was recommended that consideration be given to the routine monitoring for these parameters in Category 4, Table 1.

- "among the refineries studied, effluents were found to be relatively uniform with respect to the types of compounds detected but not necessarily the concentrations."

5.2 API Studies

While the PACE work was in progress, the American Petroleum Institute (API), in conjunction with the Environmental Protection Agency (EPA), carried out similar work in the United States (12). The study was originally initiated by EPA as part of an overall program to develop refinery effluent guidelines for toxic pollutants, reflecting the application of Best Available Technology Economically Achievable (BAT). The study had 3 objectives:

1. investigate a possible surrogate parameter toxic pollutant relationship

2. establish day-to-day variability for toxic pollutants

3. establish differences in recovery between two different analytical procedures - isotope dilution versus internal standard.

Forty-nine samples were collected over a 6 month period from two New Orleans refineries. The split samples were analyzed for the full EPA priority pollutant list using methods similar to those in the PACE studies.

A total of twenty-four organic and seven elemental priority pollutants were found during the study (15). Twenty-eight of the thirty-one pollutants detected were found at both refineries. Priority pollutants found at average concentration exceeding 100 p.p.b. in the influent samples (intakes to the treatment system) were benzene, ethylbenzene, toluene, chloroform, phenol, 2,4-dimethyl phenol, anthracene/phenanthrene, naphthalene, chromium and zinc.

Since EPA did not expect PCBs, pesticides, asbestos and TCDD in the effluent, analyses were not done for these compounds.

In the final effluent samples, chromium and zinc were detected at concentration levels ranging from 30 to 240 p.p.b. The remainder of the priority pollutants were either not detected, or detected at very low concentration (<20 µg/L or <20 ppb) in the final effluent samples. A very detailed evaluation of the EPA methodology was carried out with similar findings to those reported by PACE. Statistical analysis was not done when the results for a compound were near the detection limit and if over 50% of the results were non-detected.

The conclusions drawn by the API/EPA study were very similar to those reported by PACE. The most important are listed as follows:

- "refinery treatment systems can reduce priority pollutants present in raw wastewater to very low levels."

- "Much of the variability of final effluent concentrations is due to variability associated with the analytical methods currently available to measure effluent concentrations at the part-per- billion level."

- "The two refineries were remarkably similar with respect to the pollutants present in the influent samples and the concentrations of these pollutants."

- "continued evidence of the possibility of sample contamination with such priority pollutants as methylene chloride, benzene, toluene, chloroform and phthalates indicates that analytical data for low levels of these pollutants are subject to question."

- "The magnitude of results examined on a one at a time basis of the between-laboratory bias and the within-laboratory precision of EPA procedures 'remains a limitation of the methods' utility for regulatory purposes'."

- "The concentrations of priority pollutants in the refinery effluents studied are too low to allow a valid assessment of the utility of using traditional parameters as surrogates for priority pollutants."

On the basis of this and other work, the EPA, in their effluent limitations, guidelines, pre-treatment standards and new source performance standards (5, 15) concluded that "the most important pollutants or pollutant parameters in petroleum refinery wastewaters are:

- chromium (where zinc chromate is used as a corrosion inhibitor)
- total suspended solids, oil and grease, BOD, pH
- phenolics (4AAP), COD, sulfide, ammonia".

5.3 St. Clair River Study

Another pertinent study that involved refinery wastewater characterization from two refineries was conducted by the Ontario Region of Environment Canada with some assistance from the Ontario Ministry of Environment. This study was undertaken after the perchloroethylene spill into the St. Clair River. The wastewaters from two refineries (Imperial and Suncor) discharging into the river were collected and analyzed for a comprehensive list of contaminants including volatile, acidic and base-neutral organics (16). The study concluded that refinery effluents were not a source of volatile organics.

Chlorinated organics were found in the Suncor impounding basin samples but were also found in the intake water. The levels of aromatic compounds (benzene, xylenes) and polynuclear aromatic compounds (naphthalene, phenanthrene, fluorene, etc.) were higher in the Suncor impounding basin than in samples collected from the same site during the PACE studies. However, the report mentions

that on the day of sampling, the refinery experienced a major power failure which resulted in an emergency shutdown of part of the operation. There was also a fire in one unit area possibly when Environment Canada was taking their samples. Suncor's wastewater treatment system has been expanded in 1986 so that all wastewater from the refinery is biologically treated.

5.4 Work by Individual Refineries

Further wastewater characterization, specific to petroleum, was also carried out by four of the Ontario refineries - Shell (Sarnia), Imperial (Sarnia), Suncor (Sarnia) and Texaco (Nanticoke). These studies were oriented extensively towards a target list of pollutants.

Shell	-	3 intake grabs, 4 effluent grabs
Imperial	-	7 intake composites, 7 effluent composites
Suncor	-	2 intakes, 4 St. Clair River samples, 2 cooling waters, 2 storm waters, 2 biotreatment feed samples, 2 effluent from biotreater, 2 total effluent
Texaco	-	4 influent to biotreater and 4 effluent.

The data generated by these individual refineries were submitted to the Ontario Ministry of the Environment in May 1986. The data, along with all pertinent PACE data, have been entered into a data base inventory. It is important to note that not all the effluent samples were taken at the discharge from the biotreater clarifiers. Some effluent samples were prediluted by once-through cooling water. Print-outs of the data along with summary tables are available (upon request to the MOE).

While work is still required to comprehensively organize this data set, a summary table has been prepared to include all parameters with maximum values greater than 1 µg/L (see Table 2). The frequency of detection is also presented as a percentage.

In general, Table 2 is consistent with Table 1 which is a summary of the PACE studies. A few exceptions are noted but these must be properly examined by considering other available information:

- many of the metals detected were also routinely found in the intake waters at comparable concentrations (i.e. barium, boron, strontium and titanium)

- the detection of vanadium and titanium may require rechecking as the results were only marginally above the detection limit

- most of the volatile chlorinated compounds were detected at only one refinery and were also found in the intake waters from that refinery. Their presence was attributed to upstream sources.

- chloroform, methylene chloride and phthalates were, in all likelihood, detected due to laboratory contamination (9, 10, 11, 14, 15).

The review of these data has dramatically shown the need for a proper organization and presentation of results to allow meaningful conclusions to be drawn. The format should include the following information:

- frequency of detection
- number of determinations
- concentration levels - minimum
  - maximum
  - median
  - logarthmic - normal mean
- analytical variability
- proper identification of sample which includes analysis for conventional parameters and a brief written description of production and treatment operations.

TABLE 2: SUMMARY OF ENTIRE MOE DATABASE ON ONTARIO REFINERY EFFLUENTS

Parameter	N.A.P.	N.D.	% A.D.L.	% F.D.	M.N.	Med.	Min./Max. Values (µg/L or ppb)	
METALS								
Barium	8			100			17	180
Boron	8			75			20	580
Chromium	12			83			<5	220
Copper	12			83			<4	32
Strontium	8			100			140	4500
Titanium	8			75			8	15
Vanadium	13			54			10	20
Zinc	13			54			10	20
Zirconium	5			100			<10	60
VOLATILES								
1,1,1-Trichloroethane	21	9	29	57	3	3	2	30
1,1-Dichloroethane	20	14	10	30	2	1	3.0	9
1,2-Dichloroethane	19	12	16	37	11	1	11	140
1,2-Dichloropropane	21	15	10	29	2	1	4	15
Carbon Tetrachloride	18	12	11	33	2	1	3	20
Chloroform	21	9	19	57	3	1	2	26
Dichlorodifluoromethane	11	7	9	36			53	53
Methylene chloride	21	7	33	67	14	5	2	180
Tetrachloroethylene	10	8	20	20	4	1	2	13
Vinyl chloride	10	8	20	20	18	5	22	135
Benzene	21	7	33	67	8	1	3	64
Toluene	21	7	29	67	2	1	2	13
o-xylene	7	1	29	86	112	1	230	546
p-xylene	9	1	22	81	81	1	200	527
m-xylene	6	1	17	83	34	1	200	200
ACID EXTRACTABLES								
2,3,4,6-Tetrachlorophenol	6	5	17	17	20.8	5	100	100
2,4-Dimethylphenol	7	4	14	43	35.9	5	226	226
2,4-Dinitrophenol	8	7		13	4.5	5	-	-
Phenol	17	8	6	53	240	10	8	8
BASE-NEUTRALS								
4-Bromophenyl phenyl ether	6	5	17	17	2.1	1	7.7	7.7
Acenaphthene	19	9	16	53	2.8	1	0.017	4.2
Anthracene	17	10	18	41	3.8	1	0.13	15
Benzo(a)anthracene	19	11	11	18	3.2	1	0.026	0.11
Bis-2-ethylhexyl phthalate	9	2	78	78	23	4.8	1	120
Di-n-butyl phthalate	10	8	20	20	20	2	2	25
Di-n-octyl phthalate	11	7	18	36	4	2	3	3
Diethyl phthalate	14	12	0	14	2.1	2	0.4	1
Dimethyl phthalate	13	10	15	23	4	2	2.1	16
Fluorane	19	11	11	42	1.4	1	1.9	4
Methyl naphthalene	2	2	0	0	0.1	0.1		
Naphthalene	19	8	42	58	16.8	2	0.19	73

Note: All the above do not represent only effluent from the biological part of the treatment system. Also the detection limits varied from less than 1 ppb to 10 ppb, etc.

N.A.P: Number of Analyses for Parameter.

N.D.: Non Detected

M.N.: Mean calculated using valves at and above Detection Limits.

% A.D.L.: % measured above Detection Limit.

% F.D.: Frequency of detection was % calculated using all values which were reported as non-detected. Some of these values were reported as less than 1 and no detection limit was stated.

Med.: Median calculated using values at and above Detection Limits. Where minimum and maximum values are identical, then only one analytical result was reported above the detection level.

6.0 RECOMMENDED APPROACH TO REFINERY EFFLUENT CHARACTERIZATION AND MONITORING

As a general approach, this working group recommends the following as being the most effective and comprehensive for wastewater characterization and monitoring:

STEP 1 - Initial Characterization - a complete review of literature and existing data followed by analysis of treated and untreated wastewaters for a comprehensive list of contaminants based on priority pollutant lists. In addition, other contaminants not on the specific lists should be identified by broad spectrum instrumental scans. This will be part of a detailed interpretive report that considers the industrial processes, treatment technologies, quality of intake water and other pertinent information.

Objective - to confirm the current understanding of compounds that are present and are not present in the wastewater. At least 6 months to one year is required to complete this step.

STEP 2 - Follow-up Studies - to further verify the results of Step 1 and to reconfirm previous studies on:

- quantitation of identified compounds, in addition to those on priority pollutant lists
- variability of contaminant discharge
- fate and transformation of the key contaminants
- site specificity

Another 6 months of work (at least) is required to complete this step.

STEP 3 - Monitoring - for a group of contaminants identified by STEP 1 and STEP 2 as a means of demonstrating wastewater treatment effectiveness with respect to environmental contaminants and to establish variability over a longer period. This component is on-going and should include two groups of parameters.

- Group 1 - Control Parameters - those that are required by the waste-treatment operators to control the treatment plant.

- Group 2 - Demonstration Parameters - those that demonstrate (to the regulatory bodies and the public) that the treatment plant is effective in maintaining a high quality effluent that contains non-detectable or very low concentrations of environmental contaminants. If, after a period of time, specific parameters are continuously not detected, then they should be delisted. MOE's conceptual regulation had two different lists each with its own frequency.

- Group 3 - It is further recommended that annual characterization work be carried out for the first 3 years, particularly if a process change has been introduced, to verify that the wastewater quality has not changed significantly.

It is envisaged that STEP 3 will be a MOE regulatory requirement.

6.1 Present Status of Work by Ontario Refineries

The work carried out on refinery wastewater to date has now been more completely examined in the context of the above recommendations.

6.1.1 Characterization

The characterization work of over 36 comprehensive analyses of the final treated effluent from Ontario refineries carried out by the individual refineries and by PACE is considered to be a significant bank of information. The only deficiencies that may be identified are as follows:

- the parameter lists identified for these studies were based on the EPA priority pollutant list which is different than the ultimate Ontario effluent priority pollutant list. These lists may not always include methylated polynuclear aromatics, methylated phenols, and methylated benzenes all of which may be potentially hazardous. Furthermore, only one study involved the analysis for dioxins and dibenzo furans. These were not detected nor are they expected to be present in refinery wastewaters. Periodic characterization at each refinery can correct for this deficiency.

- two Ontario refineries were not included in any of the above studies (Petro-Canada, Oakville and Petrosar, Sarnia) but Petro-Canada was included in a very current subsequent study (final report January 1987). Petrosar's effluent has been part of a government study, summer of 1986, and their own in-house survey. The results are now available and are in close agreement with above statements and conclusions.

6.1.2 Follow-up Studies

The follow-up studies carried out on refinery wastewaters have been very comprehensive and included:

- the identification of additional (non-priority) pollutants
- examination of variability at one plant
- examination of the fate and transformation of contaminants across the treatment plant to ensure that the contaminants were being degraded.

The most significant criticism of this work was directed towards the variability study. The samples collected for this study were collected at a point where the effluent had been diluted with cooling water at a ratio of 10/90 effluent/cooling water (10). Most of the samples contained nondetectable concentrations of the contaminants under review. It was suggested by those reviewing

this study that future variability studies involve the analysis of influents to, and effluents from, the biotreatment plant along with parameters to assess the overall performance of the treatment plant (sludge age, dissolved oxygen, etc.). In this way effluent quality and variability, if observed, could be related to influent quality and/or performance of the treatment plant.

A study was recommended by the MISA Technical Committee that involved:

- two refineries - Esso (Sarnia) and Petro-Canada (Oakville)
- analysis of 6 biotreatment plant influents and 6 biotreatment plant effluents (clarifier effluent) from each refinery. Clarifier effluent was specified to address the issue of dilution. The number of clarifier samples at Esso was increased from 6 to 12 (two different time periods).
- analysis for conventional parameters and other parameters to assess performance of the two biological treatment plants.

The parameters recommended for this study were the priority pollutants from Category 3 and 4 in Table 1 of this report. It was also suggested that some volatile chlorinated compounds be added to the list because of their appearance in Table 2 of this report. Also the results would confirm the findings of past studies regarding chlorinated organics.

This study was completed in the fall of 1986 and the consultant's report was given to the MISA Technical Committee in February 1987. The report is to be made public in early 1987.

6.1.3 Monitoring

At present the Ontario refineries carry out frequent routine monitoring for the following parameters:

- pH*
- suspended solids*
- oil and grease
- ammonia nitrogen
- sulphides
- organic carbon
- total phenols*

* daily, others 3 times per week

On the basis of the PACE studies, it is felt that these parameters are sufficient to monitor the performance of the wastewater treatment plant and the general quality of the effluent with respect to present regulations. Quality is also defined by the non-detection or very low concentration (below 10 ppb) of trace organics. If further monitoring is required by regulation or voluntarily carried out by refineries for demonstration purposes, it is recommended that additional parameters selected from category 4 and if necessary category 3 of Table 1, could be added to the list. These could be monitored on a less frequent basis (those from category 4 more frequently than those in category 3). The working group agreed that a rationale for listing and delisting compounds to the two Demonstration Lists is needed. This rationale could be based on frequency of detection and concentration values. The concentration values selected for listing/delisting must be defined from biological information (toxicity and persistence), practicality of removals and ease of analytical detection.

6.2 Summary of Recommended Monitoring Approach

In summary, the recommended approach to effluent monitoring after initial comprehensive characterization work and subsequent follow-up studies have been done, is as follows:

Routine Daily Control Monitoring - for a group of parameters that assist industry with the performance of their treatment plants.

The federal and provincial list presently monitored by the refineries is more than adequate for such monitoring. In fact, a parameter such as sulphide could probably be monitored once a month. While these parameters cannot be correlated to the variability of trace contaminant levels, the quality of the treated effluent is measured by these parameters.

Demonstration Monitoring - for additional parameters to show that the treatment plants are effective in maintaining low or non-detectable concentrations of priority pollutants. The pollutants selected would be based on previous characterization work and at this stage the recommended parameters for refineries are: benzene, toluene, ethylbenzene, xylenes, chromium and zinc (chromium and zinc only if used by the refinery for corrosion control). This suggested frequency would be less than daily but more than monthly and could be reduced if continual performance is consistent (see previous remarks regarding listing/delisting mechanism).

The Working Group discussed at length two different concepts for a possible Monthly Demonstration Monitoring program. One concept, favoured by the industrial members, would involve listing based on the previous study results of final treated effluent. These are the results of final effluent quality in the PACE and subsequent studies and surveys. The second concept, favoured by the two government members would be to develop limits based on the feed to the biotreater, the Intermediate Treated Wastewaters. Occasionally biotreaters are upset and these pretreatment compounds might be found in treated effluent. This list would consist of compounds frequently detected in the feed to the biotreater.

The Working Group was not able to agree on these two concepts and therefore forward both for consideration by the MISA Technical Committee.

Periodic Characterization Monitoring - perhaps on an annual basis (or less if justified), a full characterization analysis should be carried out to demonstrate that the effluent quality is generally similar to expectations based on existing studies. It should be recognized that one characterization analysis is not conclusive in any way. However, the results will be useful as the database builds over time. The characterization list should be based on the Ontario Effluent Priority Pollutant List (EMPPL).

The Working Group discussed and agreed that criteria should be established for adding or removing compounds to any monitoring list. Time did not permit Working Group members to agree upon a formula but agreement was reached upon what factors must be considered. These factors are frequency of detection for a compound, the toxicological information, (mutagenicity, teratogenicity, carcinogenicity, acute and chronic toxicity), the persistence of the compound, the analytical accuracy for identifying and quantifying the compound, and the best available technology for specific removal of the compound.

The Working Group agreed that MOE should provide to the public within 4 weeks of receiving monitoring data an evaluation that addresses trends, consistency with past results, etc.

6.3 Monitoring and Effluent Requirements for U.S. Petroleum Refineries for Priority Pollutants

It is important to note that the above recommendations for monitoring are much more stringent than the monitoring requirements for U.S. refineries. The results of the EPA/API studies are discussed in Section 5.2 and EPA concluded from these that the concentration of priority pollutants in petroleum refinery wastewaters are a function of well operated effluent treatment systems. The biological stage of the treatment system is controlled by well known operating principles while the conventional parameters confirm past good operation. Thus, EPA set effluent limits for TSS, BOD, phenols, pH, etc., and did not set national limits for trace contaminants.

The EPA in drafting their effluent limitation regulations (5) excluded priority pollutants for one or more of the following reasons:

- non-detection in refinery wastewaters (below 10 ppb).
- already are effectively controlled by technologies upon which other effluent limitations and guidelines are based
- their detection is believed attributed to laboratory analysis and sample contamination (either during collection, transportation or analysis)
- the amount and toxicity of each pollutant does not justify developing national regulations

However, under the U.S. Clean Water Act's National Pollutant Discharge Elimination System (NPDES), petroleum refinery wastewater discharge permits have been issued, by EPA or States with delegated permit authority, which specify monitoring requirements and control limits for a number of priority pollutants. NPDES permits are established on a site-specific basis for industries discharging treated process wastewaters directly to a receiving water body. Permit writers can set monitoring and control requirements for conventional and priority pollutants using the national categorical standards for the industrial sector, using the best professional judgement procedure or for receiving water quality reasons (ie: pollutant limit is established for the effluent to ensure that the State water quality standards are not exceeded).

The permit priority pollutant requirements of 28 petroleum refineries (in 1980, there were 303 operating refineries) are summarized in Table 3. These permits are from EPA's Abstract of Industrial NPDES Permits (9) which is intended to illustrate various permitting techniques, and similarities and differences in effluent limits and monitoring frequencies. Additional permits would have to be secured from EPA or individual State permit authorities,

however, to completely assess the permit requirements of the entire U.S. petroleum refinery industry. Of the 18 priority pollutants listed in Table 3, control limits have been established for 17 of these contaminants in at least one permit. The most common monitoring frequency is once per month but this varies (see Table 3 for details).

Note that where chromium is used as a corrosion inhibitor, permits include discharge limitations for either total chromium, hexavalent chromium or both in a variety of sampling frequencies both as grab and composite samples. Twenty-three permits have chromium limits.

The information on EPA requirements is deemed important because the priority pollutant issue has been studied in the United States for a longer period of time. Valuable experience has been gained concerning the practicality of complex monitoring and the eventual use of results in legal enforcement of regulations.

TABLE 3: SUMMARY OF PRIORITY POLLUTANT REQUIREMENTS OF 28 U.S. PETROLEUM REFINERY NPDES PERMITS

Priority Pollutant	No. of Permits with Discharge Limitations (kg/day or ppb)	No. of Permits with Monitoring Requirements Only	Monitoring Frequency and Type	Permit Reference Number
aromatics	-	1	1/month grab	AK 841
anthracene	1	-	1/month 24 hr. composite	NJ 1511
benzene	3	2	1/week grab (2)	IL 1244, MI 1066
			1/month 24 hr. composite	NK 1511
			2/year 24 hr. composite	TX 4227 (runoff from Tank farm)
chloroform	1	-	1/month 24 hr. composite	NJ 1511
chromium	23	-	various grab & composite requirements	required in 23 out of 28 permits
cyanide	2	-	2/year 24 hr. composite	IL 1244, IL 2861
1,2-dichlorobenzene	1	-	1/month 24 hr. composite	NJ 1511
1,4-dichlorobenzene	1	-	1/month 24 hr. composite	NJ 1511
ethylbenzene	1	2	1/month 24 hr. composite	NJ 1511, IL 1244, IL 2861
			2/year 24 hr. composite	
			1/month 24 hr. composite	
isophorone	1	-	1/month 24 hr. composite	NK 1511
lead	3	-	3/week 24 hr. composite	IN 49751, MA 833, NJ 1511
			4/month grab composite	
			1/month 24 hr. composite	
naphthalene	1	-	1/month 24 hr. composite	NK 1511
phenanthrene	1	-	1/month, 24 hr. composite	NJ 1511
polynuclear aromatics hydrocarbons (PAHs)	-	3	2/year 24 hr. composite (2) 1/month grab	IL 1244, IL 2861, AK 841
polychlorinated biphenyls (PCBs)	1	-	1/week 24 hr. composite	IN 49751
1,1,1-trichloroethane	-	1	1/month 24 hr. composite	MI 3778 (special study)
2,4,6-trichlorophenol	1	-	1/month 24 hr. composite	NJ 1511
toluene	2	2	2/year 24 hr. composite (2)	IL 1244, IL 2861, TX 4227,
			1/week grab	NJ 1511
			1/month 24 hr. composite	
zinc	3	-	3/week 24 hr. composite	IN 49751 (refines waste
			1/month grab	lubricating oil), KY 388,
			1/month 24 hr. composite	NJ 1511

Note - phenols using the 4AAP method is considered a conventional pollutant. NJ 1511, Exxon's petroleum refining organic chemical plant has 8 unique pollutant limits (nominal 110,000 barrels per day (BPD) throughput at the refinery and nominal 80,000 BPD purchased feedstock for the organic chemical plant).

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APPENDIX A - Refinery Processes (by K. Graham A-1 to A-25)
B - Refinery Wastewater Treatment, Individual Refinery Data B-1 to B-8)
C - Analysis Methods Used for Studies, C-1 to C-4.

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APPENDIX A

PETROLEUM REFINING

Prepared by K. Graham, Suncor

PETROLEUM REFINING

Introduction

To begin with, it is important to realize that the design features of a Refinery such as the selection of metallurgy, and types of process units used are essentially a function of two factors:

1) the crude oils being processed, and
2) the types of petroleum products in demand.

The crude oils may be of natural origin (found in underground formation) or synthetic (produced from tar sands) and these will vary widely in quality and chemical composition depending on their source.

We should keep two things in mind regarding crude oils, ie.:

1) Every single crude oil from a field location, whether separated from its neighbor by a few hundred yards horizontally or vertically, is a highly individual, unique chemical mixture which cannot be matched exactly by any other crude oil.
2) Most Canadian crude oils are blends of the production from several fields.

The market decides what hydrocarbon molecules are required to meet consumer demand and these may or may not be contained in the crude oil being processed. Due to these differences in both crude oils and product slate every Refinery is unique and different.

Crude Oils

Crude oils are a complex mixture of hydrocarbons, ie. chemical compounds made up of Hydrogen (H) and Carbon (C) ranging from the simplest hydrocarbon, Methane (CH_4) to compounds that are solid at room temperature such as high molecular weight asphaltenes. More than 3000 chemicals have been identified in crude oil by Chemists and these are but a small portion of the total number present.

Crude oils also contain impurities such as sulfur, nitrogen and oxygen compounds, along with some heavy metals and inorganic salts.

Crude Oil - Chemical Composition

Due to a wide variety of chemical hydrocarbon species contained in crudes, the petroleum industry has learned to live with a set of empirical measurements and customer acceptance tests containing some physical and chemical properties of the crude and select boiling range fractions.

A crude assay will include a relationship between true boiling point and the volume or weight of crude oil distilled. This allows the refiner to collect the distilled portions into "cuts" or fractions for separate analysis. Although a crude of high API gravity would normally be expected to yield more distillate and less residue than one of lower gravity, there is no precise correlation and many anomalies occur. This happens partly because crudes vary considerably in the relative proportions of light oil (gasoline, kerosene and diesel). Also, because the gravity of a crude is not only dependent on the boiling range distribution of its components (TBP curve) but on the hydrocarbon composition of the fractions.

Another way of differentiating crudes is by hydrocarbon type.

Hydrocarbon Designation

Crude oils are broadly classified by hydrocarbon composition as paraffinic, naphthenic, asphaltic or mixed base crude oils.

Paraffinic base crude oils contain paraffin wax, but little or no asphaltic materials. These crudes consist mainly of paraffinic hydrocarbons and usually give good yields of paraffin wax and high-grade lubricating oils. This type of crude is not prevalent in Canada.

Naphthenic base crude oils contain little or no paraffin wax, but asphaltic material is usually present in large proportions. These crudes

consist mainly of naphthenes (cyclic hydrocarbon compounds) and yield lubricating oils that are more viscosity sensitive to temperature than those from paraffin base crudes. Special refining methods make it possible to produce naphthenic base lube oils from crudes other than naphthenic.

Asphaltic base crude oils contain little or no paraffin wax but asphaltic substances are present in large proportion.

Mixed base crude oils contain substantial amounts of both paraffin and asphaltic material. Both paraffins and naphthenes are present together with a certain proportion of aromatic hydrocarbons. Most crudes are of this type, exhibiting a considerable amount of chemical overlapping.

Sweet and Sour Crudes

Another method used to designate crude oils is based on the chemical nature of the sulfur impurities present. Crudes that contain hydrogen sulfide in solution or mercaptan compounds, ie. weak acids, are called sour crudes as compared to sweet crudes.

Sweet crudes may have sulfur present in the form of monosulfides, disulfides, cyclic sulfides or complex ring structures. These compounds are not as malodorous as hydrogen sulfide or mercaptans.

Refinery Classification

As stated earlier, Refineries differ widely in size, number of process units and degree of process sophistication. Each Refinery is different and dependent on its crude and product mix. To assist in differentiating between various types of Refineries a broad classification system has emerged. In the jargon of the industry, Refineries are designated as Topping, Cracking or Conversion and those incorporating lube oil and petrochemical manufacture. The majority of Canadian Refineries are Conversion Refineries.

Refinery Processes

Although many different process units can be used to convert crude oil into on-specification products, the processes themselves can be broken down into the following categories:

1) Separation
2) Conversion
3) Treating
4) Blending

1) Separation

The most common method for separating oil into fractions is distillation. To a lesser degree separation technologies such as solvent extraction and crystallization are also used but are limited in their applications.

2) Conversion

Conversion processes are used to change the size or shape of the hydrocarbon molecules to those of higher economic value. Typical examples of conversion units are Catalytic Crackers (breaking down large molecules, into smaller ones), Catalytic Reformers and Isomerization Units (reorganizing molecules) and Alkylation/Polymerization (joining two molecules together).

3) Treating

Many of the sulfur, nitrogen and oxygen compounds found in the crude oil are to a lesser or greater degree contained in the various fractions or intermediate product streams. These impurities are removed or modified by treating processes such as desulfurization, denitrification or chemical (caustic or acid) treating.

4) Blending

Fuel products in the gasoline and distillate range are a blend of a variety of hydrocarbon fractions produced by a number of process units in the Refinery.

For example, motor gasoline may be a blend of butane, straight run naphtha, reformate, catalytically-cracked gasoline, thermally-cracked or coker gasoline, alkylate and additives.

Crude Oil Distillation (Atmospheric and Vacuum)

Crude oil frequently contains brine from underground deposits. To minimize the fouling and corrosion of crude oil furnaces and distillation equipment, the crude is usually processed through a unit called a desalter. This unit removes the inorganic salts contained in the oil before it enters the distillation column.

Distillation is used to separate the crude oil into various boiling range fractions or "cuts". The basic process involves heating the crude and feeding it to a vertical distillation column where the lighter (lower boiling point) fractions vaporize and then condense out. The various fractions are continuously drawn from the tower and diverted for further processing or use as finished products.

Atmospheric Distillation

Atmospheric distillation involves the physical separation of hydrocarbon components into fractions, or intermediates of a specified boiling temperature range, by distillation and steam stripping at slightly above atmospheric pressure.

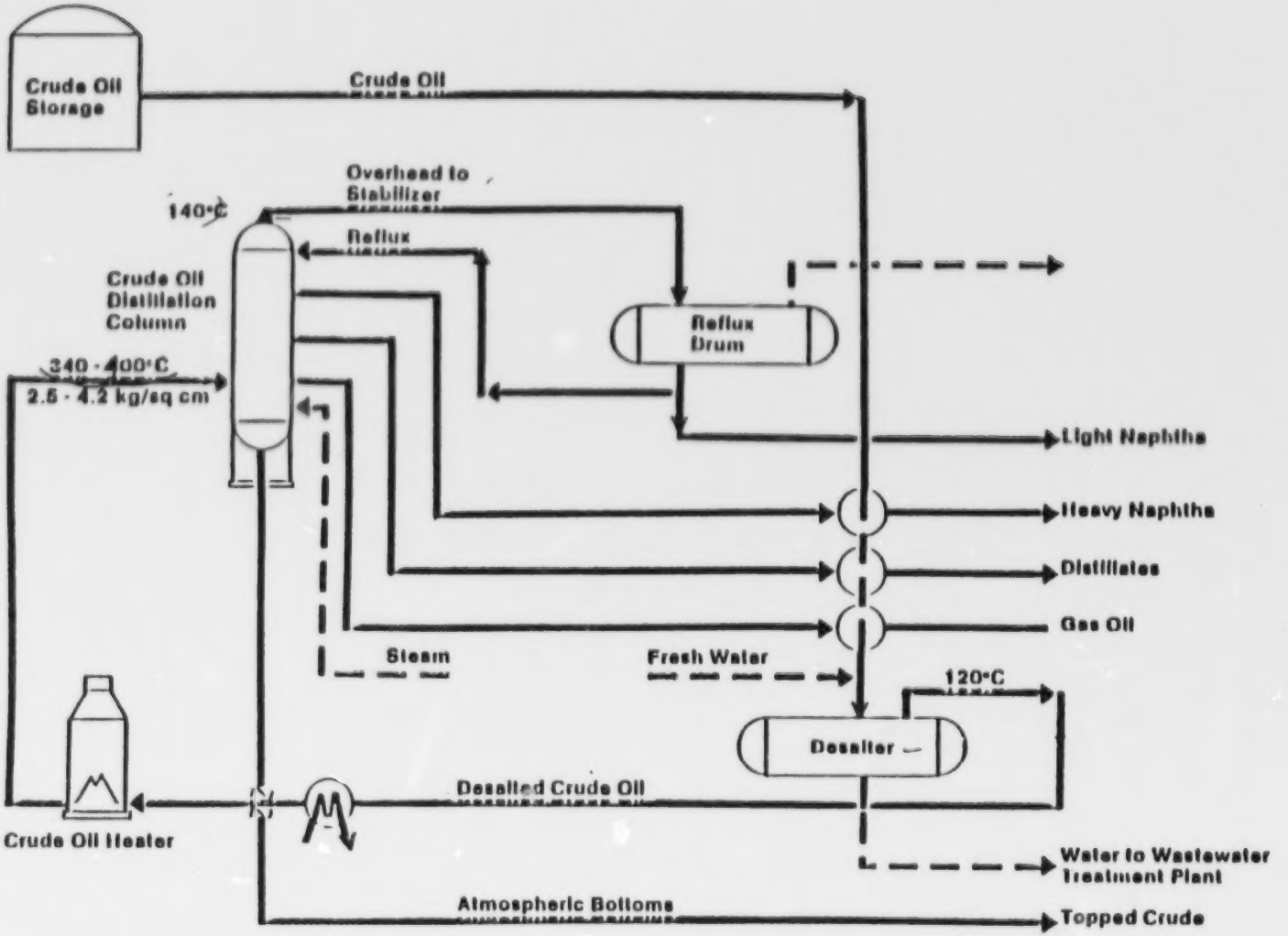
The major processing equipment items include the heat exchanger preheat train, direct fired furnace, atmospheric distillation column, and side stream product stripping columns. Fig. 1 is a schematic of a crude oil distillation unit.

Desalted crude is preheated in the heat exchanger train by recovering process heat. The preheated crude is then charged to a direct-fired furnace where additional heat is supplied to achieve partial vaporization of the crude petroleum. Both the liquid and vaporized portions are charged to the atmospheric fractionator at a temperature of about 340-400°C (650-750°F).

The crude charge is separated into several petroleum fractions within the atmospheric fractionator. A naphtha and lighter stream is taken from the tower overhead where it is condensed, and the non-condensable light ends are treated and/or recovered in other Refinery units. Several liquid sidestream fractions are withdrawn from the fractionator at different elevations within the tower. These fractions are charged to sidestream product strippers where lighter hydrocarbons are stripped off and returned to the fractionation tower. The stripping medium is either steam, light petroleum gases, or reboiler vapors.

The fractions withdrawn from the atmospheric tower are progressively heavier as they are taken from the fractionator at successively lower points. The end point of the heaviest sidestream product closely corresponds to the crude's temperature as charged to the fractionator. Fractionator bottoms (topped crude) is the heaviest petroleum fraction and is the charge to the vacuum distillation unit.

CRUDE OIL DISTILLATION UNIT



This tower produces low, intermediate, and high boiling products, such as fuel gas, naphtha, kerosene, distillate or diesel oil, gas oil and topped crude.

Naphtha is further processed to improve octane rating or is used as a petrochemical feedstock.

Intermediate boiling range products include kerosene, distillates and gas oils.

Kerosene may be chemically sweetened or hydrogen treated and sold directly as jet fuel or sent to fuel blending.

Distillates may be hydrogen treated, hydrocracked, catalytically-cracked or sold as diesel or fuel oil.

Gas oil may be sold as fuel oil, hydrogen treated, hydrocracked, catalytically-cracked, or blended.

The high boiling stream, reduced crude or straight run residue is usually fed to the vacuum distillation unit for further gas oil recovery.

Steam injected into the tower to enhance the distillation process condenses with the column overhead product into wastewater having a high dissolved organic content.

This water and similar steam condensates from other fractional distillation processes forms the stream requiring biological treatment in wastewater treatment systems.

Water from desalting operations also must receive biological treatment.

Sour water is steam stripped to remove sulfur and ammonia. Sulfur is reclaimed by the sulfur unit.

Vacuum Distillation

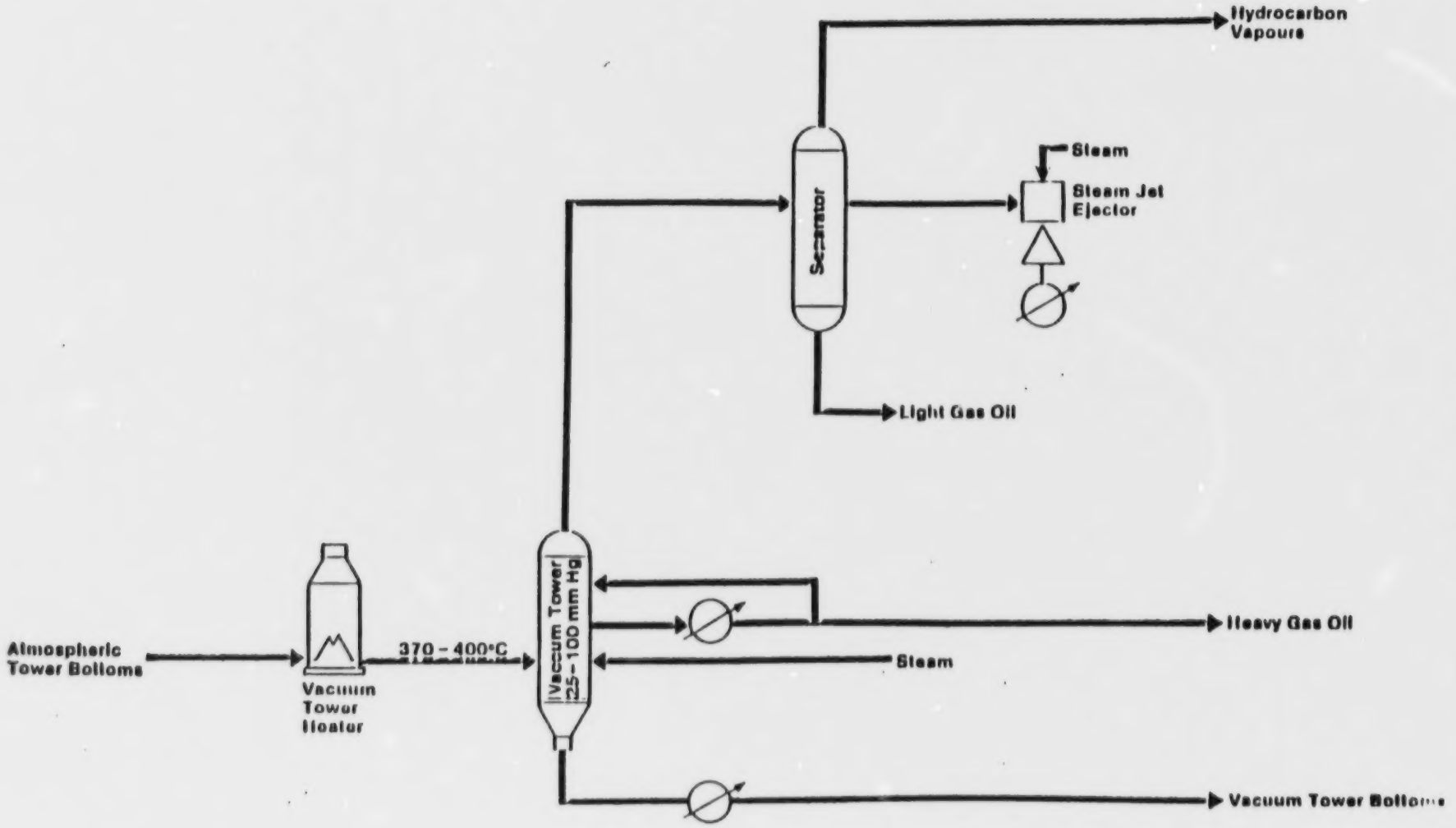
When crude oil is heated to temperatures above 370-400°C (at atmospheric pressure), undesirable thermal decomposition or thermal cracking takes place. To avoid this, the streams that boil above 340°C (650°F) such as atmospheric column bottoms (reduced crude) are separated in a second distillation tower operated under vacuum.

Vacuum distillation separates the residue from the atmospheric crude column into a heavy residual pitch and one or more heavy gas oil streams. Under vacuum the extremely high temperatures (cracking) necessary to produce these heavy distillates by atmospheric fractionation is avoided. A vacuum distillation unit is shown in Fig. 2.

The vacuum gas oil product may be used for several purposes eg. it may be sent to a catalytic cracker, thermal cracker or hydrocracker to be cracked into a gasoline blending stock. The choice of these options may be limited by the crude characteristics and/or the existing Refinery design.

The residuals from vacuum distillation may be sent to the asphalt plant, coking unit or be directly blended into a bunker fuel.

VACUUM DISTILLATION UNIT



Conversion Processes

Three types of conversion processes are commonly used in a Refinery to upgrade intermediate products into higher value products. These are classified by what they do to the hydrocarbon molecules in the feed ie. breaking down or cracking, re-arranging or combining.

Cracking processes break large hydrocarbon molecules into smaller, lower-boiling point molecules. The usual products of cracking are gaseous hydrocarbons, gasoline blending stocks, gas oil, fuel oil, and coke. Typical cracking processes include catalytic cracking, hydrocracking, and viscosity breaking or coking (both thermal cracking processes).

Re-arranging processes are those in which the molecules are changed to form a product of different characteristics, usually converting straight chain hydrocarbons into aromatics which have higher octane values. The most widely used re-arranging process is catalytic reforming.

Combining processes join together olefinic and paraffinic molecules that are recovered from thermal and catalytic cracking to produce more valuable gasoline blending stocks. Two processes normally utilized are alkylation and polymerization. Alkylation combines the olefins with isobutane while polymerization joins two olefin molecules together.

Catalytic Cracking

The Fluid Bed Catalytic Cracking (FCC) process is one of the most versatile and widely used in the refining industry. The process uses a solid, finely powdered zeolitic catalyst that when mixed with a gas has transport properties similar to those of a liquid.

Feedstocks to the FCC Unit can vary from distillate boiling-range materials to vacuum residuals. Products include, liquified petroleum gases (LPG), olefins, a high octane gasoline component and fuel oil blending stock.

An example of a straight chain paraffin hydrocarbon breaking down into an olefin and a smaller paraffin is shown as follows:

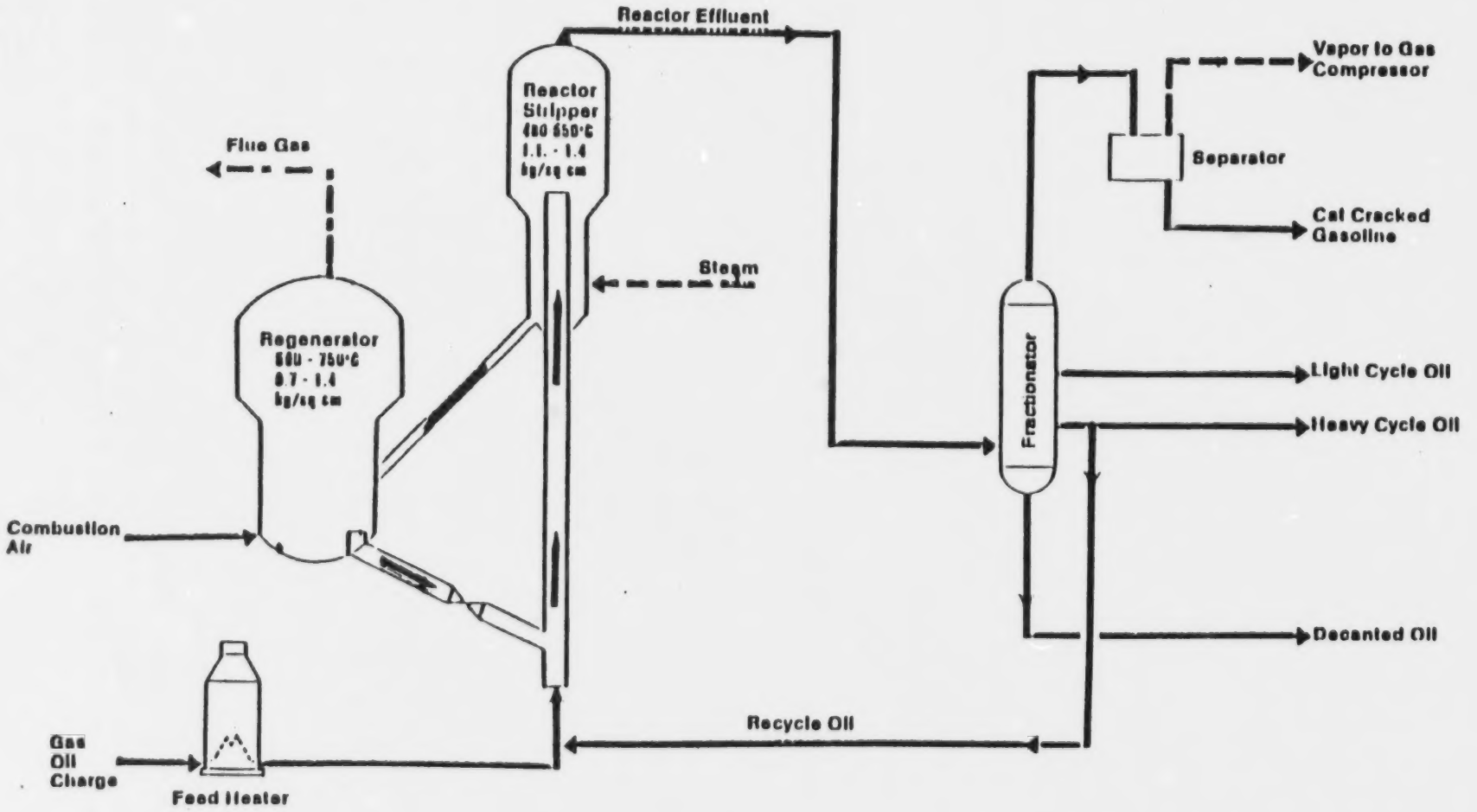
$$C_{14}H_{30} \xrightarrow[900_{\circ}F+]{\text{Catalyst}} C_8H_{18} + C_6H_{12}$$

Tetra-Decane — Iso-Octane + Hexane

The process is commonly used to convert heavy vacuum gas oils and coker gas oils to lighter products, to produce higher value gasoline and distillate blending stocks.

A typical fluid bed catalytic cracker is shown in Fig. 3.

FLUID CATALYTIC CRACKING UNIT



The reaction products are generally separated by distillation into an overhead product of gasoline boiling range and lighter components, a middle product of light cycle oil and a bottoms product of heavy cycle oil (decant oil).

The overhead product is further fractionated to yield LPG, olefins and debutanized gasoline. The light cycle oil can be hydro-treated and used as a distillate blending component or used as feed to a hydrocracking unit. The heavy cycle oil is processed to concentrate entrained catalyst in one portion which is recycled to the riser. The clarified heavy cycle oil is highly unsaturated, aromatic oil that can be used in a variety of ways notably in the manufacture of carbon black.

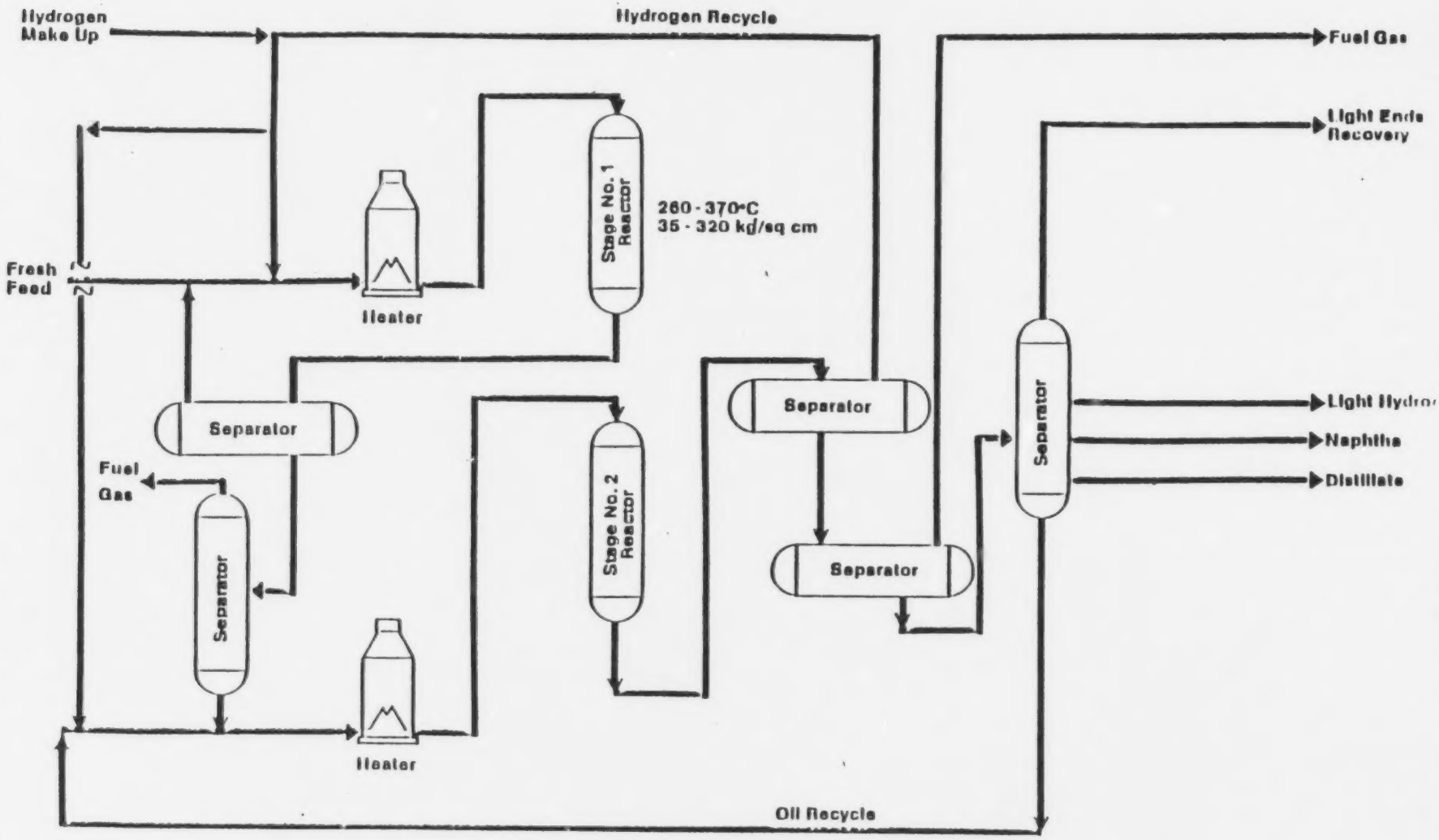
Hydrocracking

Hydrocracking is a combination of catalytic cracking and hydrogenation. Heavy feedstocks are converted into lighter fractions in a high temperature, high pressure reaction in the presence of hydrogen and a catalyst. Hydrocracking is generally used to supplement the catalytic cracking process. A hydrocracker costs more to build and operate than a fluid bed catalytic cracker. However, by using hydrogen, the hydrocracker can handle heavier fractions and cracked gas oils which are considered not amenable to catalytic cracking. The primary feed to the hydrocracking unit, is generally light cycle oil from the cat cracker.

The hydrocracker can employ either one or two reactor stages. A unit designed to treat a feed of relatively low sulfur and nitrogen content and low unsaturate or aromatic composition can utilize a single reactor. If the feed is relatively high in sulfur, nitrogen, unsaturates, and aromatics, two reactors are required. The first reactor functions as a hydrodesulfurizer, converting sulfur and nitrogen into hydrogen sulfide and ammonia which are removed in a separator before charging the feed to the second stage. A typical two-stage hydrocracker is shown in Fig. 4.

Reactor effluent passes through high and low pressure separators to remove hydrogen which is recycled, and light components. The hydrocracking process can yield a variety of products including saturated light ends such as normal and isobutane, a light gasoline fraction for blending, a naphtha fraction for reformer feed, a high quality kerosene for jet fuel, or distillate for diesel and home heating fuel. Heavier material is recycled. Some refiners recycle anything heavier then naphtha to extinction.

TYPICAL TWO-STAGE HYDROCRACKER UNIT



Viscosity Breaking

Historically, thermal cracking antedates catalytic and hydrocracking. It is an older process and the quality of the products made from this process is poorer and therefore require treatment or upgrading.

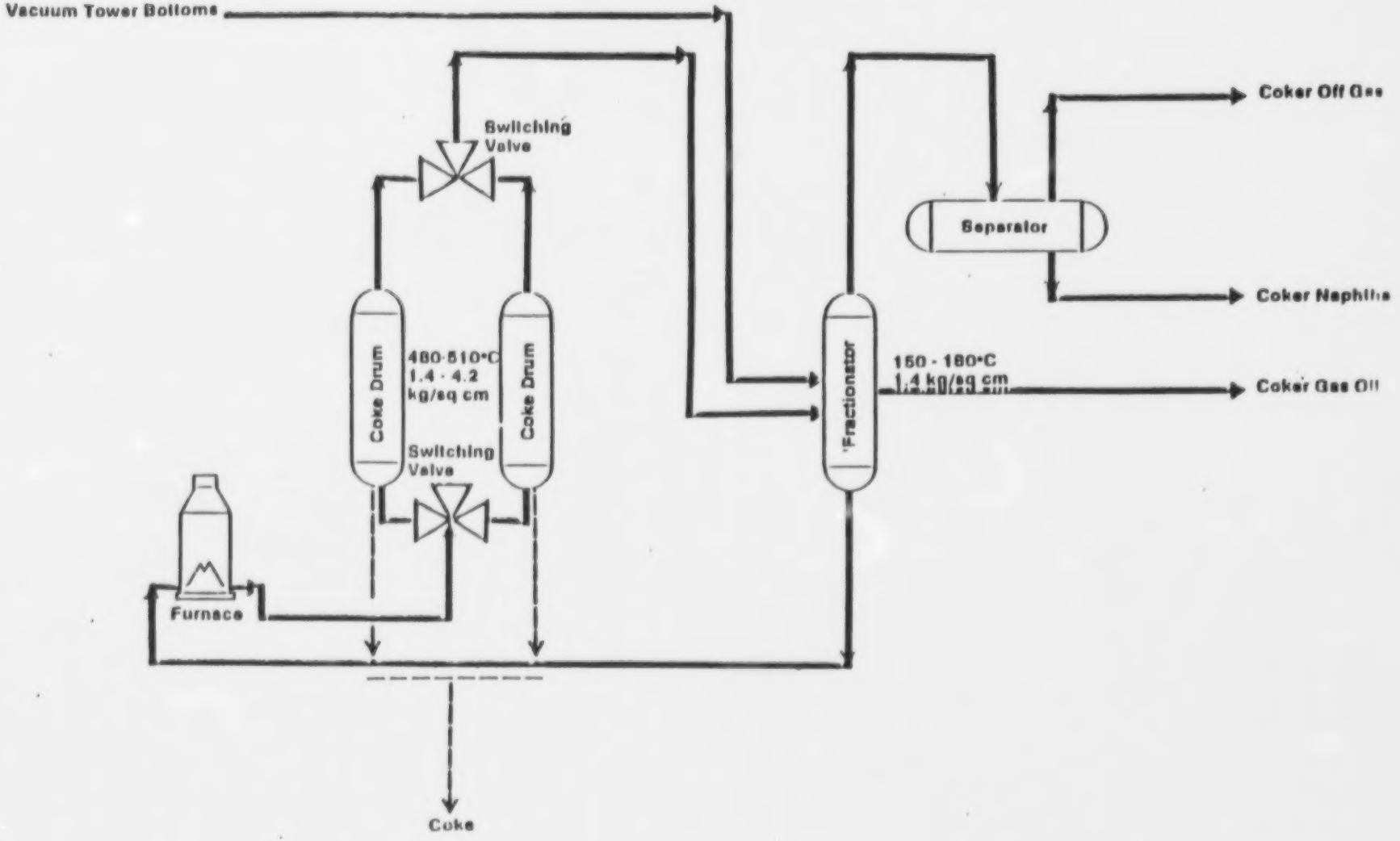
The visbreaking process employs thermal cracking of heavy residual oils (pitch) under mild conditions to reduce the viscosity or pour point of the charge stock. The feed to the unit is heated and thermally cracked in the visbreaker furnace. Cracked products are quenched with gas oil and flashed. The vapor overhead is separated into light distillate products while the liquid is processed in a fractionator, some operating at a vacuum, to recover a heavy distillate. Some refiners blend this distillate with fuel oil while others use it as catalytic cracking feed. The residue or tar from the fractionator is generally used for coker feed.

Coking

Coking is a thermal cracking process in which crude oil residue (vacuum residuals) and other decanted oils and tar-pitch products are cracked at high temperature and low pressure into lighter products and petroleum coke. The objective is to produce gas oil and lighter petroleum stocks that can be charged to catalytic or thermal crackers from the residum.

There are two principle coking processes called fluid or delayed, and their use is limited to only a few refineries in Canada.

DELAYED COKING UNIT



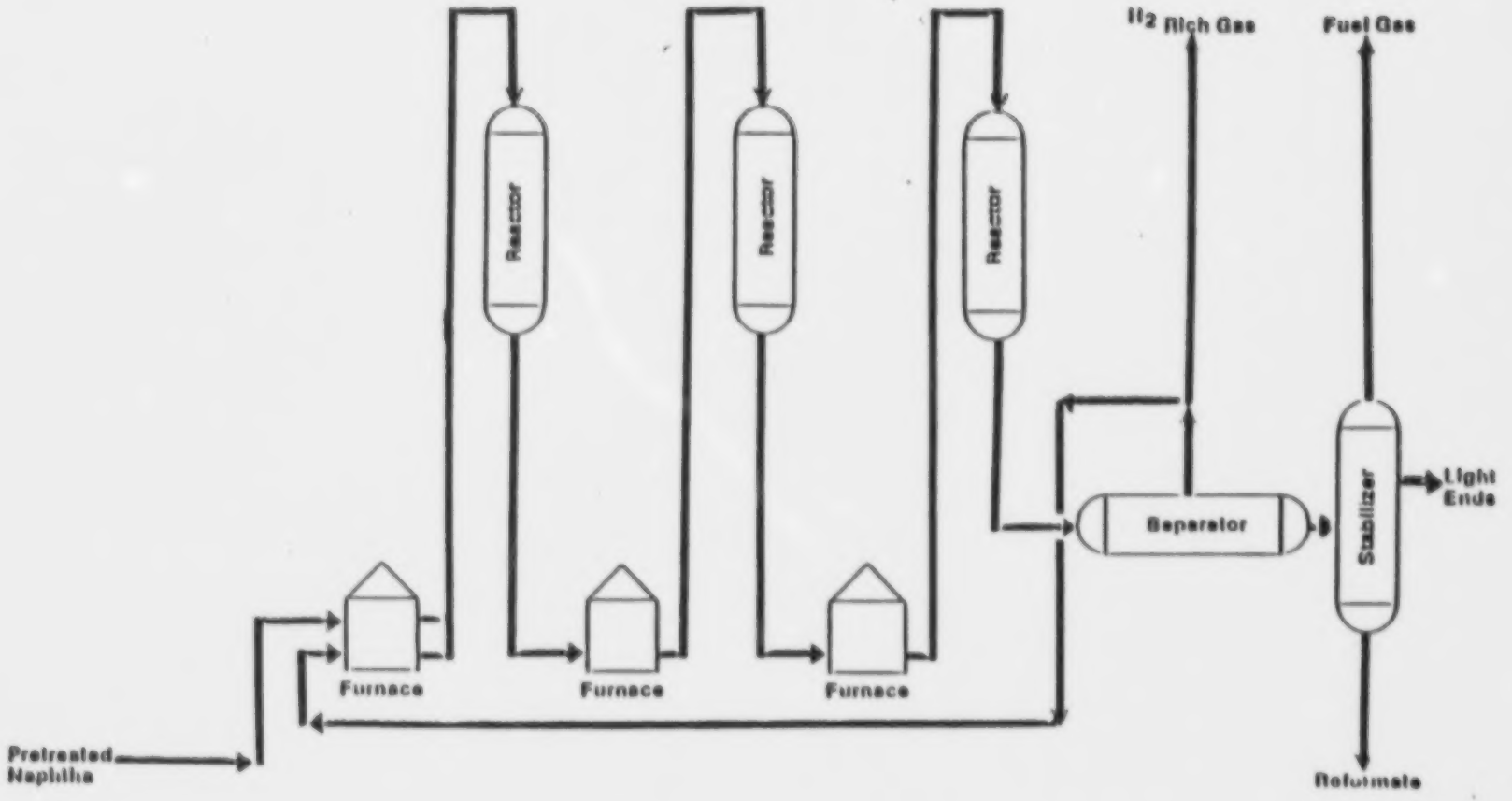
Catalytic Reforming

One of the most important units for generating high quality gasoline components is the Reformer. Cracking processes previously discussed are designed to increase the availability of gasoline and at the same time reduce heavy fuel oil. In this portion of our presentation we will detail a process that takes in feedstock already in the gasoline range, called heavy straight run naphtha. It is a low octane material typically around 50-60 Research Octane Number. By reforming its octane it can be increased to above 90 clear RON.

The flow diagram of a typical fixed bed semi-regenerative Reforming Unit is shown in Fig. 5. Reformer catalyst are alumina based coated or impregnated with active noble metals such as platinum and contain specified amount of chlorine and/or fluorine. These latter materials are present in small amounts, less than 1%. There are many refineries today using catalysts that combine a second noble metal with the platinum to enhance selectivity and yield.

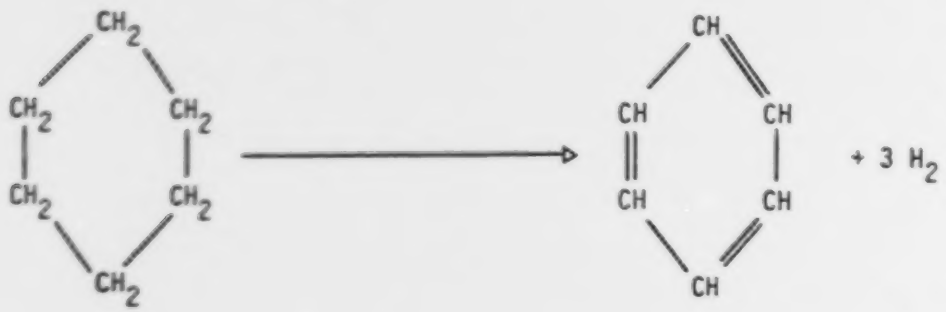
After continuous operation over a period of from six to twelve months, the catalyst activity declines to such an extent that operation becomes inefficient and regeneration or replacement with fresh catalyst becomes necessary. If the spent catalyst cannot be regenerated at the unit, it is returned to the manufacturer where the platinum is recovered, and replacement is made with fresh catalyst.

CATALYTIC REFORMING UNIT



The reforming process requires an atmosphere of hydrogen to prevent the severe deposition of coke of the catalyst. Fortunately, hydrogen is one of the main products of reaction.

There are a number of reactions which take place, one of which is the conversion of naphthenes to aromatics by removal of hydrogen atoms. The reactions is endothermic so the outlet temperature of the reactor is lower than the inlet. A typical reaction is:



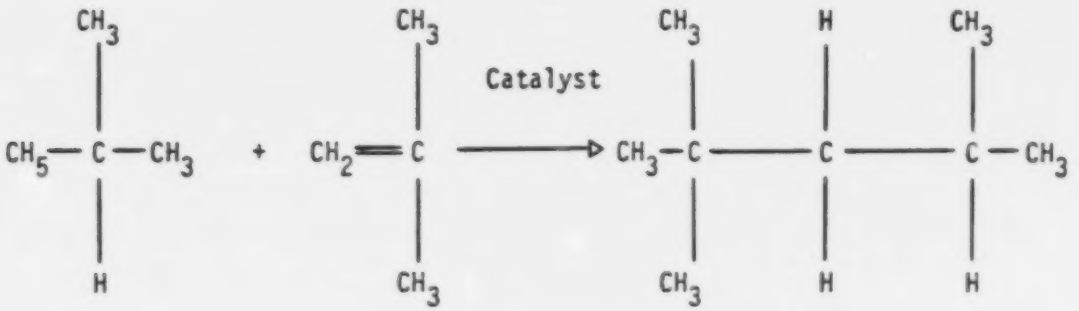
Cyclohexane Benzene Hydrogen

Alkylation

Alkylation units are used to produce a high octane component for gasoline blending from C_3 and C_4 streams contained in the Cat Cracking unit's off gases.

Alkylation is the chemical combination of two hydrocarbon molecules to form one molecule of higher octane rating. An olefin (propylene, butylene, and amylene) and an iso-paraffin (usually isobutane) are catalytically reacted using either 98% sulfuric acid or 75-90% hydrofluoric acid to produce a high

octane component known as alkylate. The reaction is shown as follows:



Isobutane Isobutylene Iso-octane

The hydrofluoric acid alkylation unit is shown in Fig. 6.

A dry olefinic feed is mixed with excess isobutane and contacted with the liquid catalyst in the reaction vessel. The reactor effluent is separated into hydrocarbon and acid phases in a settler with the acid being returned to the reactor. The alkylate is then processed further.

Both the sulfuric acid and hydrofluoric acid processes include distillation sections of varying configurations to separate the alkylate product from excess isobutane, normal butane and propane. The isobutane is returned to the reactor section. Normal butane and propane are removed from the process and used for LPG.

Reactor effluent from the sulfuric acid process is utilized in a refrigerant cycle to cool the reactors. Acid and organically combined sulfur in the reactor effluent are removed by caustic scrubbing before distillation. The alkylate, normal butane, and propane products from the distillation section are also caustic scrubbed.

a) Sulfuric Acid Process

The sulfuric acid alkylation process is a catalytic process of

combining molecules of butylenes with isobutane (some propylene and amylenes may also be present) in the presence of 98% sulfuric acid (catalyst) to form molecules of iso-octane. The product, called alkylate, has one of the highest anti-knock ratings of any refinery product. In general, alkylate is the most important component of high octane aviation gasoline blends.

Structurally, this is what happens to the arrangement of carbon atoms in these molecules during alkylation: Sulfuric acid alkylation units usually are operated at 60-100 psig. Temperature is an important variable in alkylation. If the temperature is allowed to exceed 70°F in sulfuric acid alkylation, acid consumption is increased and yield and quality are decreased. Therefore, sulfuric acid alkylation facilities are equipped with extensive refrigeration systems. Reaction temperatures in the order of 40°F are fairly common. The sulfuric acid catalyst becomes quite viscous if the temperature gets much lower than this.

The hydrocarbon feed is dried, cooled and mixed with 98% acid before entering the top of the reactor time tank. The volume ratio of isobutane to butylenes may be varied all the way from 3-1 to as much as 15-1. The product withdrawn from the bottom of the reactor contains suspended acid, most of which separates out. Any acid still remaining in the product is neutralized with caustic soda. The recovered acid strength gradually decreases, due mainly to dilution with oil and water. The spent acid (about 89% acid) is used elsewhere in the Refinery or returned to the manufacturer for refortification. The hydrocarbon feedstock is desulfurized. The sulfur compounds otherwise combine with sulfuric acid and increase it consumption.

The withdrawn product is sent to a debutanizer for separation of unreacted butane and isobutane. The debutanized bottoms, crude, alkylate, proceeds to a finishing unit where light ends (pentane and lighter) are removed. Then the crude alkylate is split to remove the heavier fraction, alkylate bottoms, which is further separated into motor gasoline, solvents, and fuel oil. The finished alkylate is removed to storage.

Kellogg has a sulfuric alkylation process called "cascade". At least two units are in operation in Canada.

b) Hydrofluoric Acid Process

Universal Oil Products (UOP) and Phillips licence an alkylation process catalyzed with hydrofluoric acid (HF). The typical process flow diagram is shown in fig. 6. The dried desulfurized propylene, butylene and isobutane feed is contacted with HF acid in a stirred contactor. Cooling water is sufficient to remove the heat of reaction. This process is not as sensitive to temperature as sulfur acid catalyzed alkylation. Octane numbers of the alkylate is frequently marginally lower than that made with sulfur acid catalyst.

Acid consumption is low if the feed is dry since water is rejected from the acid in an acid regenerator column as a bottom product constant boiling mixture (about 45% HF). Lower isobutane to olefin recycle ratios can be tolerated in the reactor. If the reaction temperature is too high, HF consumptions will increase because the intermediate product of the reaction, an organic fluoride is more soluble in butane. This material is absorbed on alumina.

The alkylate is predominantly C_8 but a full range of paraffinic material from C_5-C_{12} can usually be determined.

HYDROFLUORIC ACID ALKYLATION UNIT

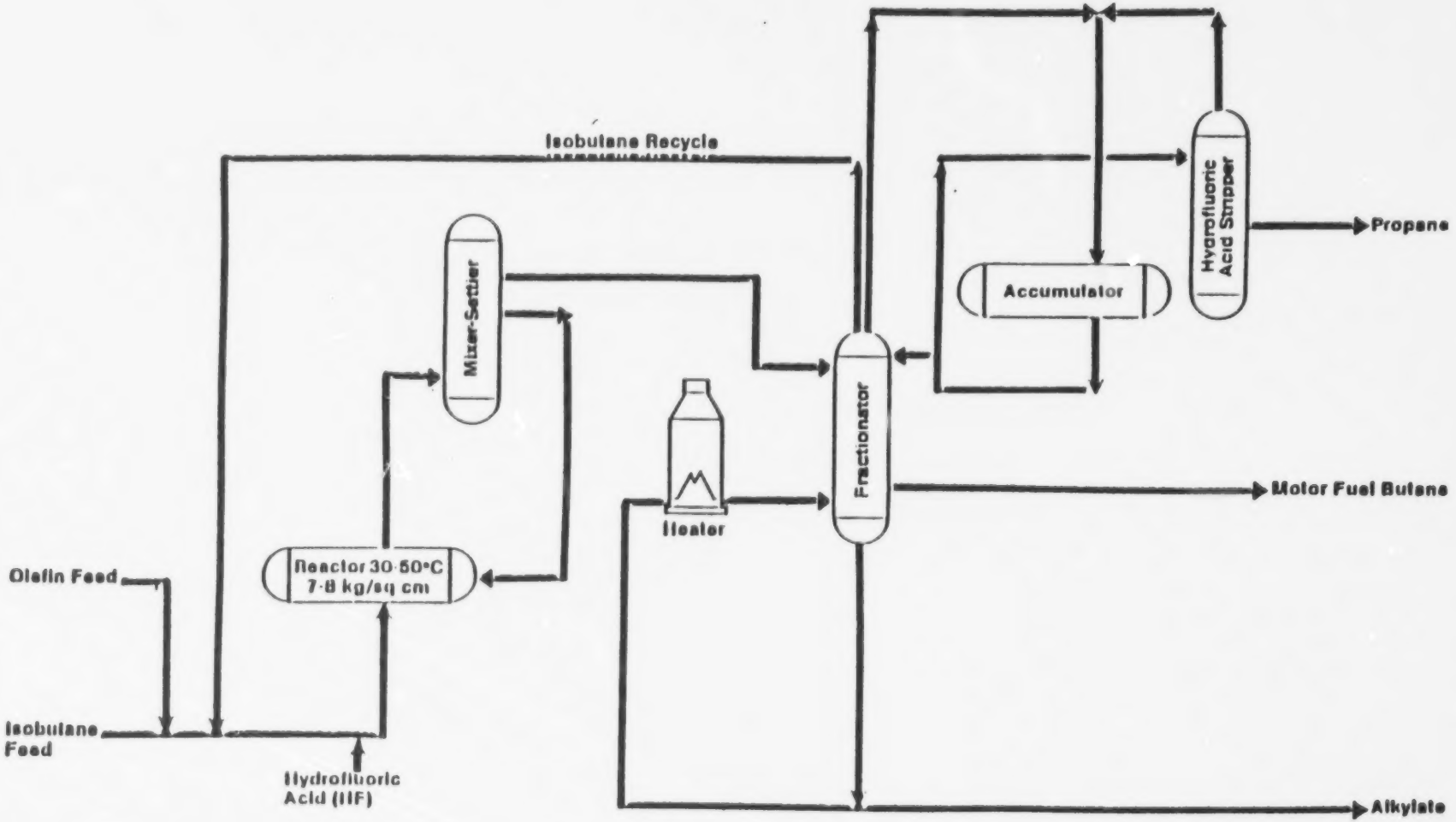


TABLE 4: ONTARIO REFINERY PROCESSES

Refinery & Location	Desalter	Crude Unit	Hydrogen Treaters	Catalytic Reformer	Crackers			Lubricating Oil
					Catalytic	Thermal	Hydrogen	
Esso, Sarnia	Yes	Yes	Yes	Yes	Yes	Yes	-	Yes
Petro Canada, Clarksom	Yes	Yes	Yes	Yes	-	-	-	Yes
Petro Canada, Trafalgar	Yes	Yes	Yes	Yes	Yes	-	-	-
Petrosar, Corunna	Yes	Yes	Yes	-	-	Yes	-	-
Shell, Sarnia	Yes	Yes	Yes	Yes	Yes	-	Yes	-
Suncor, Sarnia	Yes	Yes	Yes	Yes	Yes	-	Yes	-
Texaco, Nanticoke	Yes	Yes	Yes	Yes	Yes	-	-	-

APPENDIX B

Refinery Effluent Measurement, Sampling, Analyses and Treatment

Refinery Wastewater Treatment – Description..... B–1a & b

Esso Petroleum, Sarnia..... B–2

Petro Canada, Mississagua..... B–3

Petro Canada, Trafalgar..... B–4

Petrosar (Polysar), Corunna..... B–5

Shell, Corunna..... B–6

Suncor, Sarnia..... B–7

Texaco, Nanticoke..... B–8

CODE

Normal Flow

Recycle Flow

Emergency Bypass

REFINERY WASTEWATER TREATMENT

All Ontario refinery wastewaters are treated in a similar manner involving:

- Primary Treatment - Oil Separation
- Intermediate Treatment - Usually dissolved air flotation
- Biological Treatment followed by clarifiers
- Tertiary Treatment (in some refineries).

A brief description of these refinery systems is provided below.

Oil Separation:

The purpose of the gravity oil/water separator in refinery wastewater treatment is the separation of free oil from the water phase. The free oil may be in dispersed particle (globule) form or floating on the surface of the wastewater. Through operating experience and research programs, the American Petroleum Institute (API) developed a standardized design practice for the separation of oil from water for refinery application now referred to as an API separator. Oil removal in the context of priority pollutant removal is important because:

- volatile and base/neutral compounds associate preferentially with the oil phase thus enhancing overall removal (the recovered oil is processed into products).
- oil removal is required to avoid interference with the biological treatment processes used for biochemical oxygen demand (BOD) and phenolics removal and which provides effluent polishing to remove trace organics.

Air Flotation:

Dissolved Air Flotation (DAF) is used for the removal of suspended solids and oily materials from refinery wastewaters. The waste flow or a portion of effluent is pressurized in the presence of sufficient air

to approach saturation. When this pressurized air-liquid mixture is released to atmospheric pressure in the flotation unit, minute air bubbles, which attach themselves to and become enmeshed in the floc particles. The air-solids mixture rises to the surface, where it is skimmed off and reprocessed.

It is postulated that dissolved air flotation assists in the removal of organic priority pollutants by:

- removal with the oil phase as occurs in the gravity separators
- removal by volatilization

Neutralization and Equalization

Best removal of trace organics in biological treatment occur when micro-organism have a consistent and stable feed. The quality is somewhat controlled by neutralizing (pH range control) and equalizing. Equalization may also dampen flow variations.

Biological Treatment:

Biological treatment involves the removal of organics by micro-organisms present as a biological sludge. The organic material is consumed by the micro-organisms and converted to carbon dioxide and water. Oxygen and nutrients are required and a new cell mass is synthesized continuously and becomes acclimatized to the waste. The activated sludge process is a continuous system in which flocculated biological growths are mixed with wastewater and aerated. The biological growths are then separated from the treated waste by settling. The settled flocs are recirculated for admixture with additional waste.

With biological treatment, organic pollutants are removed from wastewaters by:

- enmeshment in and/or adsorption on the biological floc (sludge)
- biological degradation
- air stripping (from aeration)

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

ESSO PETROLEUM, SARNIA

MEASUREMENT

INTAKE - not measured (estimated from pump curves)

FINAL EFFLUENT - calculated (sum of upstream measurements) & once-through - cooling water based on intake pump curves)

MEASURED & RECORDED - flow from each API separator (3) in effluent treatment system
- flow from 2 package biological cells on sour water stripper effluent

SAMPLING

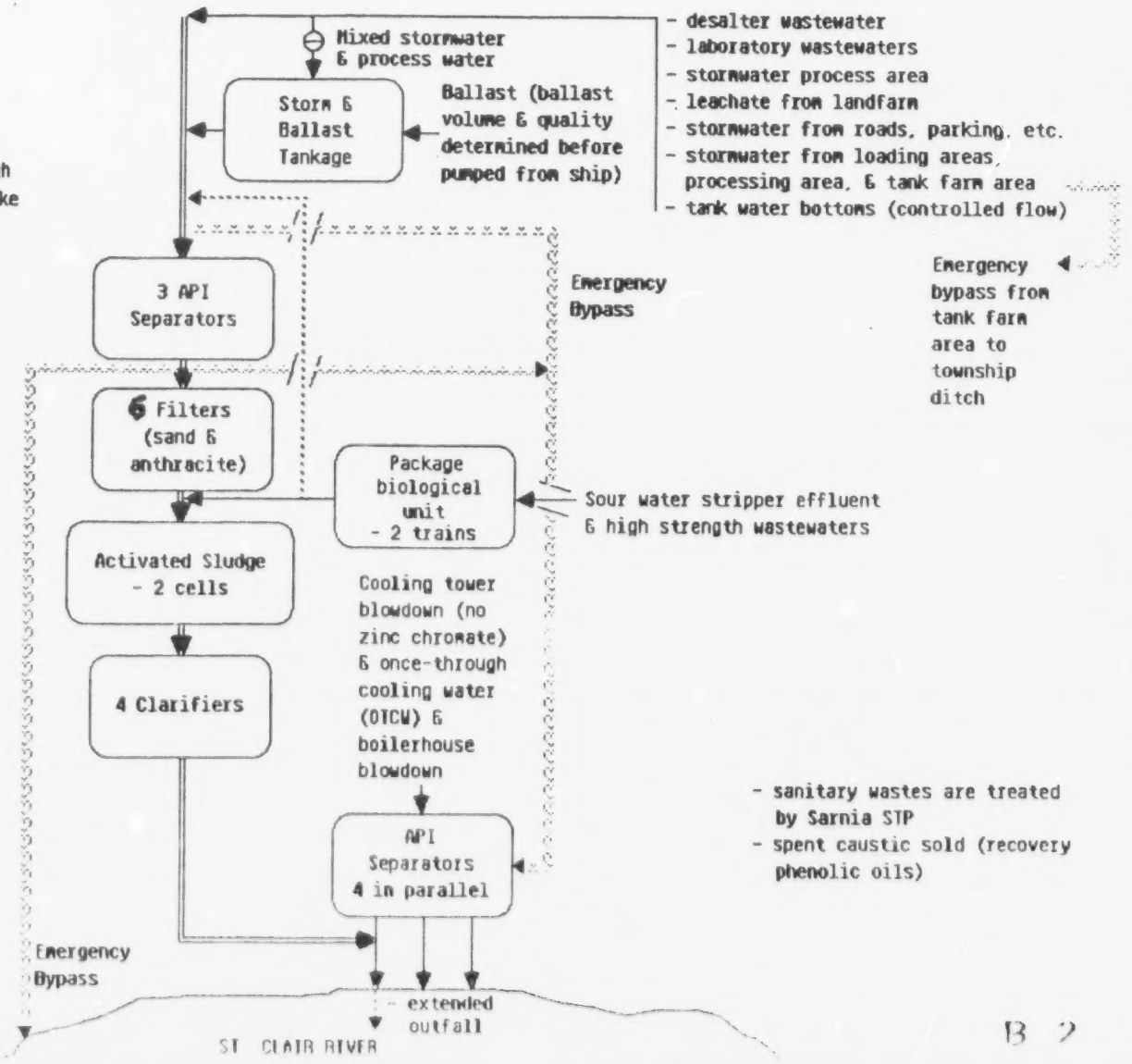
- 24 hour composite/day for 7 days/week of treated effluent after clarifiers and same for once-through cooling water (lab analyzes composite, based on flow, of cooling water samples)
- fixed time - fixed volume composite

ANALYSES

- each sample can include oil and grease, TSS, phenolics, sulphides, NH3, pH, TOC
- once/month 24 hour static fish toxicity

SAMPLING POINTS

- effluent from 4 clarifiers
- effluent from 4 OTCW separators


Mixed stormwater & process water
Storm & Ballast Tankage
Ballast (ballast volume & quality determined before pumped from ship)
- desalter wastewater
- laboratory wastewaters
- stormwater process area
- leachate from landfarm
- stormwater from roads, parking, etc.
- stormwater from loading areas, processing area, & tank farm area
- tank water bottoms (controlled flow)
Emergency Bypass from tank farm area to township ditch
3 API Separators
Emergency Bypass
6 Filters (sand & anthracite)
Package biological unit - 2 trains
Sour water stripper effluent & high strength wastewaters
Activated Sludge - 2 cells
Cooling tower blowdown (no zinc chromate) & once-through cooling water (OTCW) & boilerhouse blowdown
4 Clarifiers
API Separators 4 in parallel
Emergency Bypass
- extended outfall
ST CLAIR RIVER

- sanitary wastes are treated by Sarnia STP
- spent caustic sold (recovery phenolic oils)

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

PETRO-CANADA, MISSISSAGUA (CLARKSON)

MEASUREMENT

INTAKE - not measured
FINAL EFFLUENT - from clarifiers by Parshall flume & flow integrator
- once-through - cooling water - each measured by own weir (2)
- stormwater from final basin - intermittent discharge - integrator on flow - Parshall flume

SAMPLING

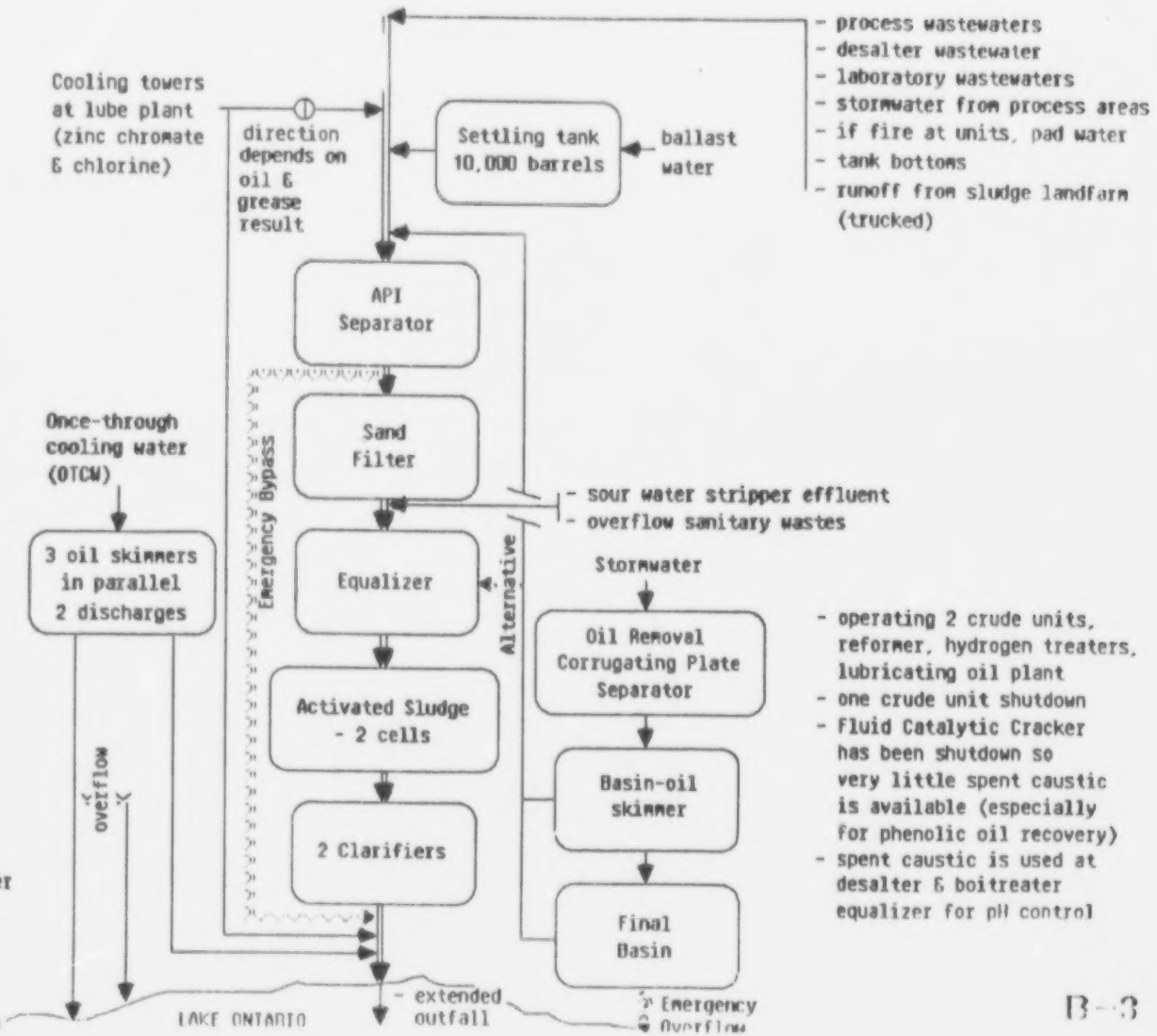
24 hour composite/day - equal volume (15 minute interval) - 7 days/week for treated process effluent
- once per week for OTCW
- stormwater - (due to intermittent discharge - a grab is as good as composite - sheen on water noticed before a detected oil and grease result)

ANALYSES

- daily: oil and grease, TSS, phenolics, sulphides, NH3, pH for process wastewaters
- inlet of sand filter and outlet of equalizer - daily: oil & grease, phenolics, sulphides
- once/month: 24 hour static fish lethality test
- oil & grease, phenolics for OTCW

SAMPLING POINTS

- inlet of sand filter & outlet of equalizer by operators for control
- outlet of both clarifiers (includes cooling water blowdown)
- discharge of once-through cooling water
- stormwater from final basin if discharged



- operating 2 crude units, reformer, hydrogen treaters, lubricating oil plant
- one crude unit shutdown
- Fluid Catalytic Cracker has been shutdown so very little spent caustic is available (especially for phenolic oil recovery)
- spent caustic is used at desalter & boitreater equalizer for pH control

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

PETRO-CANADA, TRAFALGAR (OAKVILLE)

MEASUREMENT

INTAKE - not measured

FINAL EFFLUENT - flow meter & integrator

MEASURED - flow to effluent treatment system API separator by Parshall flume
- flow to Induced Air Flotation Separator by venturi meter

SAMPLING

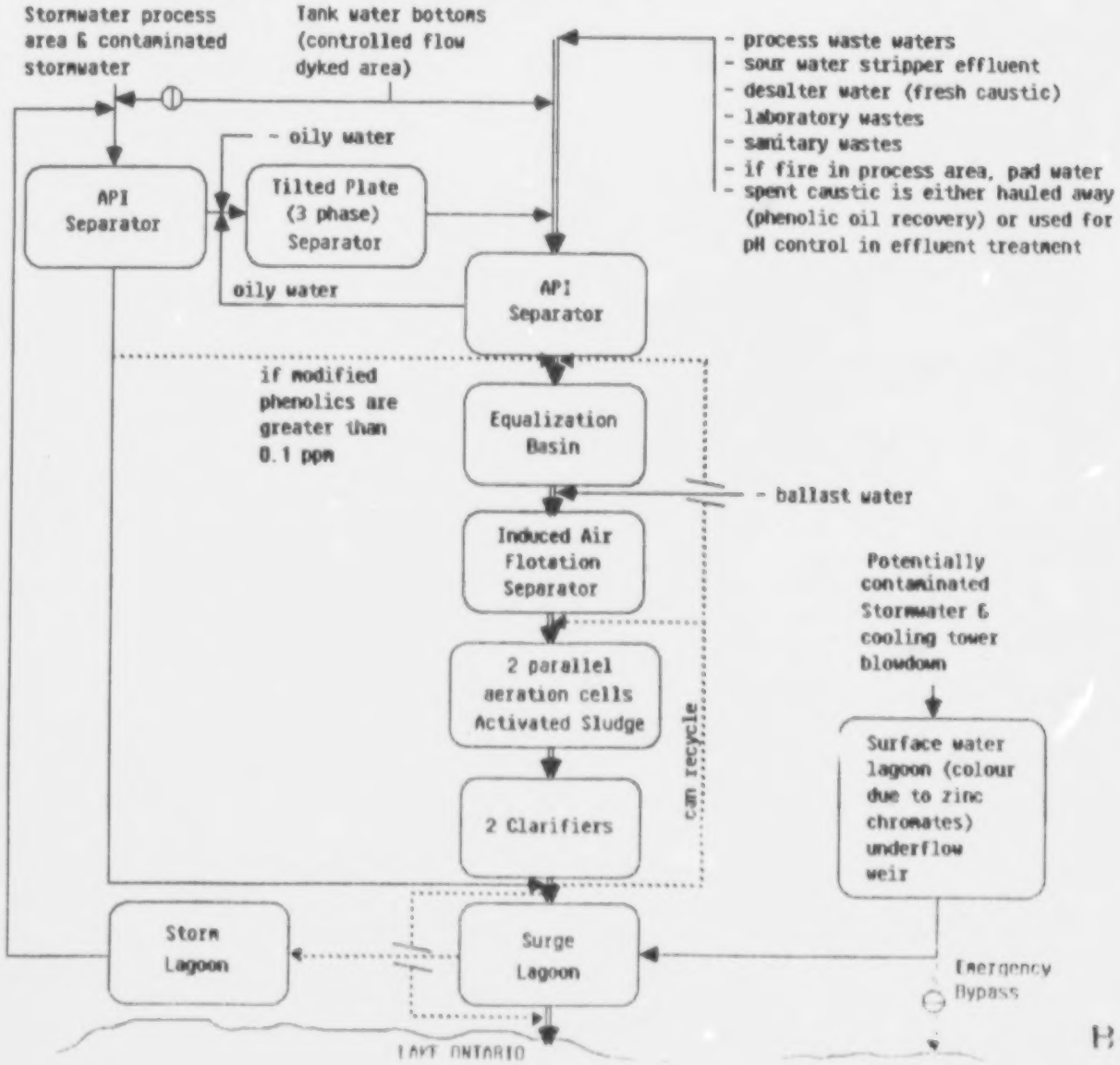
- final effluent - 24 hour composite/day for 4 weekdays (sample every 30 minutes)
- but 72 hour composite for weekend (sample every 2 hours)

ANALYSES

- operator - every 4 hours - sulphides, pH, modified phenolics final effluent into aeration cells and contaminated stormwater
- lab - final effluent 3/week - oil & grease, TSS, NH3, phenolics, sulphides, COD
- once/month 24 hour static fish toxicity

SAMPLING POINTS

- outlet API Separator prior to equalization basin (pH, phenolics, sulphides)
- inlet & outlet Induced Air Flotation
- final effluent from surge lagoon
- outlet of clarifiers


Stormwater process area & contaminated stormwater
Tank water bottoms (controlled flow dyked area)
- process waste waters
- sour water stripper effluent
- desalter water (fresh caustic)
- laboratory wastes
- sanitary wastes
- if fire in process area, pad water
- spent caustic is either hauled away (phenolic oil recovery) or used for pH control in effluent treatment
- oily water
API Separator
Tilted Plate (3 phase) Separator
oily water
API Separator
if modified phenolics are greater than 0.1 ppm
Equalization Basin
- ballast water
Induced Air Flotation Separator
2 parallel aeration cells Activated Sludge
2 Clarifiers
can recycle
Potentially contaminated Stormwater & cooling tower blowdown
Surface water lagoon (colour due to zinc chromates) underflow weir
Storm Lagoon
Surge Lagoon
Emergency Bypass
LAKE ONTARIO

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

PETROSAR (POLYSAR), CORUNNA

5 Effluent Systems - uncontaminated stormwater, oily wastes, chemical wastes, sanitary & landfarm

MEASUREMENT

INTAKE - measured by orifice plate recorded & integrated (used for net loading calculation)

FINAL EFFLUENT - orifice plate, recorded & integrated; effluent from final pond is pumped

Treatment flows for control purposes
- chemical unit system - combined flow by Parshall flume to equalizer, orifice flow to DAF, magnameter flow from DAF, flow from clarafier by Parshall flume, flow to each activated carbon cell by orifice plate and orifice plate on flow from each carbon cell

SAMPLING

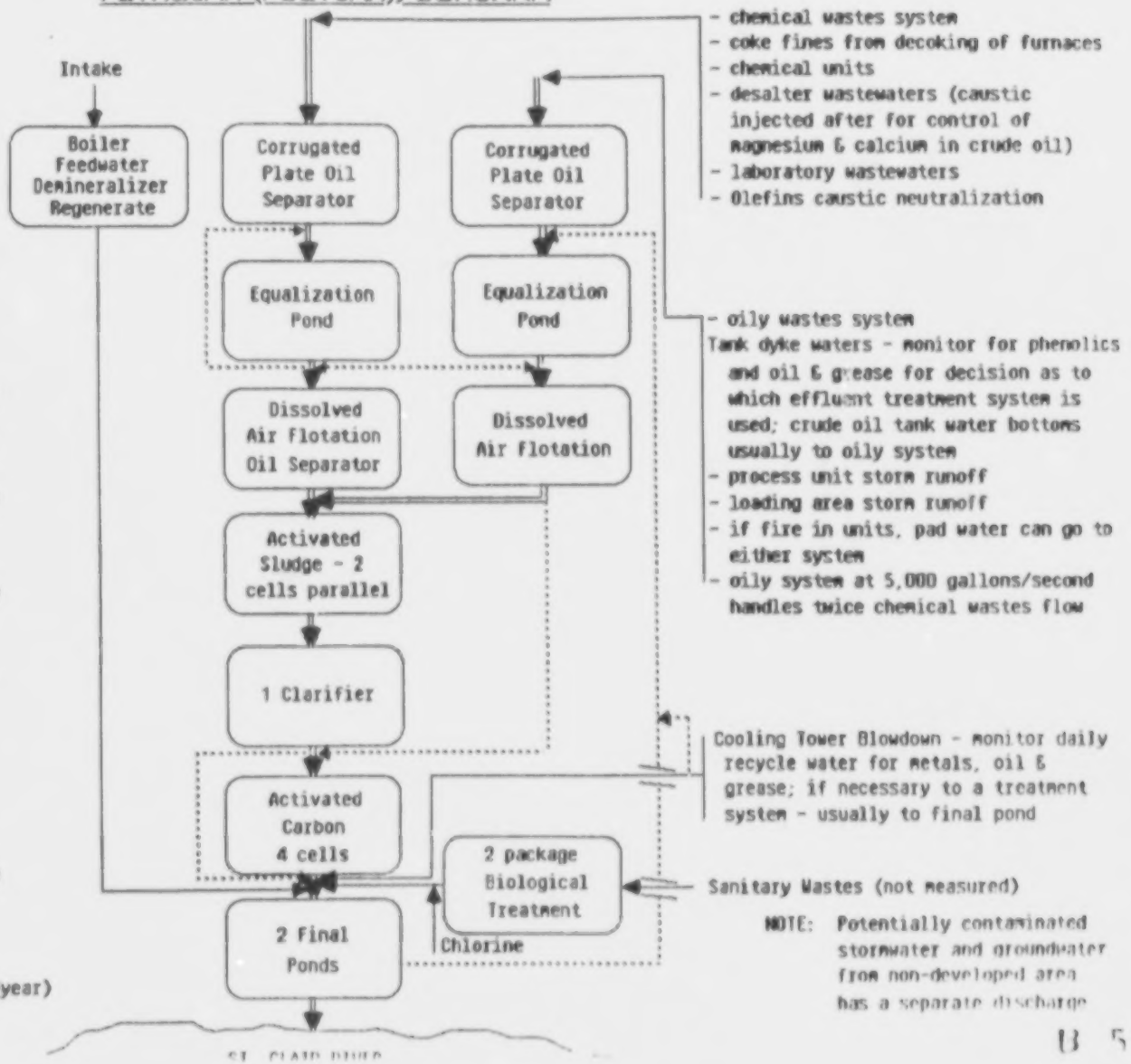
- 24 hour flow proportional composite/day for 7 days per week of final effluent at pumps
- operator control of system - 2 samples per 12 hour shift usually within treatment system

ANALYSES (final ponds)

- each composite - TSS, phenolics, TOC, NH3, oil & grease, pH, chromium, zinc
- sulphide 3 times per week
- once/month 24 hour static fish toxicity

SAMPLING POINTS

- discharge from final ponds
- leachate sludge landfarm (5 to 6 times/year)
- potentially contaminated stormwater


Intake
Boiler Feedwater Demineralizer Regenerate
Corrugated Plate Oil Separator
Corrugated Plate Oil Separator
Equalization Pond
Equalization Pond
Dissolved Air Flotation Oil Separator
Dissolved Air Flotation
Activated Sludge - 2 cells parallel
1 Clarifier
Activated Carbon 4 cells
2 package Biological Treatment
2 Final Ponds
Chlorine
- chemical wastes system
- coke fines from decoking of furnaces
- chemical units
- desalter wastewaters (caustic injected after for control of magnesium & calcium in crude oil)
- laboratory wastewaters
- Olefins caustic neutralization
- oily wastes system
Tank dyke waters - monitor for phenolics and oil & grease for decision as to which effluent treatment system is used; crude oil tank water bottoms usually to oily system
- process unit storm runoff
- loading area storm runoff
- if fire in units, pad water can go to either system
- oily system at 5,000 gallons/second handles twice chemical wastes flow
Cooling Tower Blowdown - monitor daily recycle water for metals, oil & grease; if necessary to a treatment system - usually to final pond
Sanitary Wastes (not measured)
NOTE: Potentially contaminated stormwater and groundwater from non-developed area has a separate discharge

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

SHELL, CORUNNA

MEASUREMENT

INTAKE - pump curves & amperage
FINAL EFFLUENT - by calculation (sum of DAF & Chemical Plant flows)
MEASURED - potentially contaminated cooling water from API Separator by calibrated channel
- flow from Dis. Air Flotation by Parshall flume
- flow from chemical plant by orifice meter
- water to Ethyl Corp.
- stormwater overflow (Parshall flume & automatic sampler)

SAMPLING

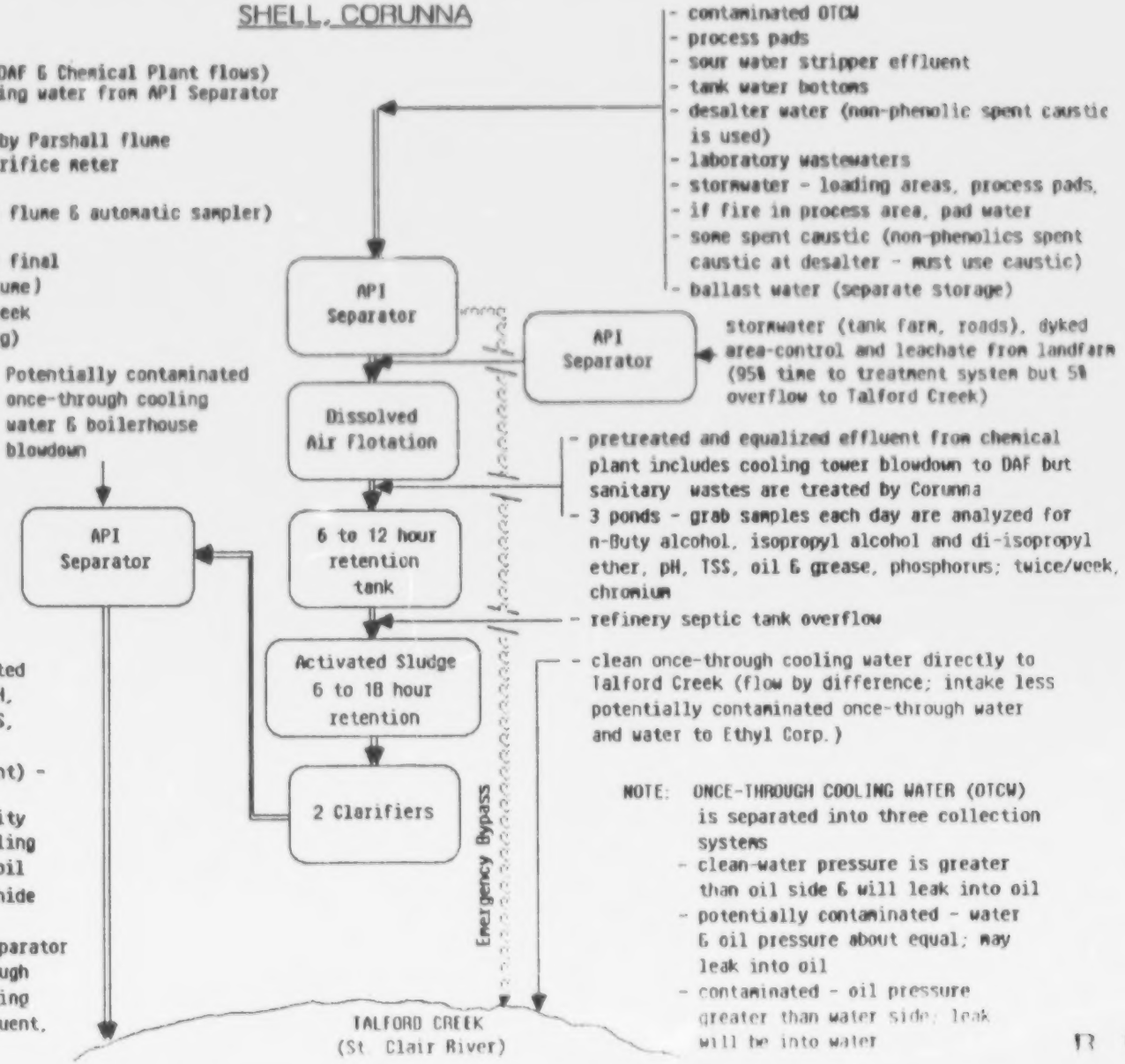
- 24 hour composite/day, 7 days/week for final clarifier (equal time/equal sample volume)
- 24 hour composite/day but 5 days per week after stormwater overflow (when flowing) and potentially contaminated once-through cooling water
- 48 hour composite continuous of biotreater feed, flow of pretreated chemical plant wastewaters, intake water and clean once-through cooling water

ANALYSES

- phosphorus- once/week inlet to biox
- clarifier composite - daily: pH, oil & grease, phenolics; 3/week: TOC; 1/week: TSS, NH3, sulphide
- for stormwater & potentially contaminated once-through cooling water - daily: pH, phenolics, oil & grease; once/week: TSS, TOC, NH3, & sulphide
- feed to biox (includes chemical effluent) - BTX analysis once/week
- once/quarter 24 hour static fish toxicity
- inlet water and clean once-through cooling water samples - daily: phenolics, pH, oil & grease - weekly: TSS, NH3, TOC, sulphide

SAMPLING POINTS

- outlet of clarifiers, outlet of API Separator for potentially contaminated once-through cooling water, clean once-through cooling water, biofeed (includes chemical effluent, pretreated chemical plant effluent


- contaminated OTCW
- process pads
- sour water stripper effluent
- tank water bottoms
- desalter water (non-phenolic spent caustic is used)
- laboratory wastewaters
- stormwater - loading areas, process pads,
- if fire in process area, pad water
- some spent caustic (non-phenolics spent caustic at desalter - must use caustic)
- ballast water (separate storage)
API Separator
API Separator
stormwater (tank farm, roads), dyked area-control and leachate from landfarm (95% time to treatment system but 5% overflow to Talford Creek)
Potentially contaminated once-through cooling water & boilerhouse blowdown
Dissolved Air Flotation
- pretreated and equalized effluent from chemical plant includes cooling tower blowdown to DAF but sanitary wastes are treated by Corunna
- 3 ponds - grab samples each day are analyzed for n-Buty alcohol, isopropyl alcohol and di-isopropyl ether, pH, TSS, oil & grease, phosphorus; twice/week, chromium
API Separator
6 to 12 hour retention tank
- refinery septic tank overflow
Activated Sludge 6 to 18 hour retention
- clean once-through cooling water directly to Talford Creek (flow by difference; intake less potentially contaminated once-through water and water to Ethyl Corp.)
2 Clarifiers
Emergency Bypass
TALFORD CREEK
(St. Clair River)

NOTE: ONCE-THROUGH COOLING WATER (OTCW) is separated into three collection systems
- clean-water pressure is greater than oil side & will leak into oil
- potentially contaminated - water & oil pressure about equal; may leak into oil
- contaminated - oil pressure greater than water side; leak will be into water

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

SUNCOR, SARNIA

MEASUREMENT

INTAKE - measured by a pilot tube (1981)
in-the-pipe device for cooling water only

FINAL EFFLUENT - Parshall flume - impounding basin flow
Parshall flume - combined flow from clarifiers ($.5 million in 1986) - recorded & integrated

Other Measurements
- ballast water from tank
- from process DAF to activated sludge
- flow to each clarifier (2 different size maintain correct hydraulic load)
- sludge return to each cell

SAMPLING

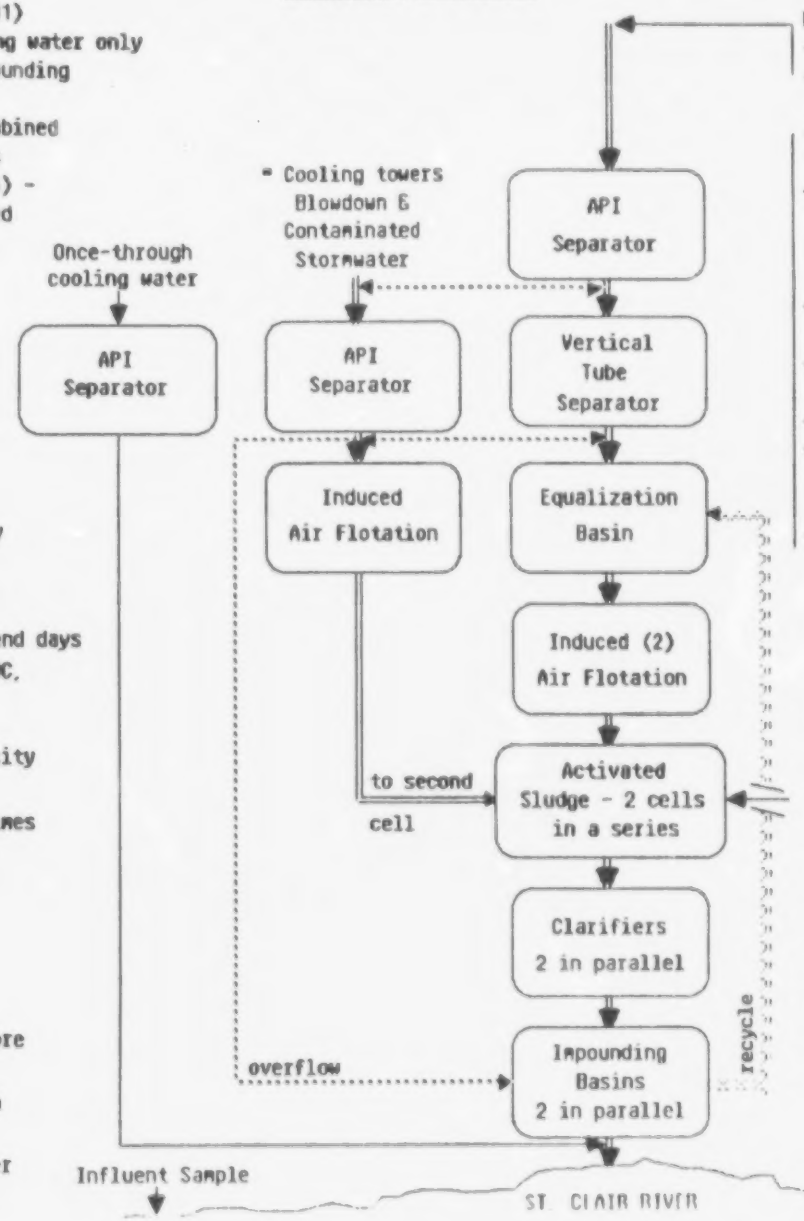
Intake - grab

final Effluent - 24 hour composite/day
7 days/week
- fixed volume sample

ANALYSES
- 5 for each weekday and 1 for 2 weekend days
- TSS, phenolics, oil & grease, pH, TOC, NH3-N for each sample
- sulphide 1 week
- once/month 24 hour static fish toxicity

SAMPLING POINTS

Operators sample and test usually 4 times per shift for pH and phenolics (ppm)
- inlet Vertical Tube Separator
- inlet Induced Air Flotation
- outlet aeration cell No. 1
- outlet aeration cell No. 2
- outlet of each clarifier (2)
- outlet of each impounding basin before dilution
- outlet API Separator in once-through cooling water
- outlet API Separator on cooling water blowdown



Process System
- sour water stripper effluent
- desalter wastewater from its own H2S stripper
- laboratory wastewaters (either system)
- if fire at units, process pad sewers

NOTE: steam purchased from Dow; condensate used as process water; small steam trim boilers

- ballast water preheated by condensate can go to either system process/contam.
- go to contaminated system if heat is needed in second biox cell
- can pump contaminate in ballast tank
- 24.5 hrs. retention time within process treatment system (API separator to clarifiers normal flow)
- to ensure that recycle pumps (20 feet below surface) always work, some recycle goes on continuously

Landfarm leachate remote from main area of refinery - discharge 3 to 4 times a year to surface runoff - could be trucked to treatment - checked for conventionals before discharge

effluent from central septic tank

Operator tests every 4 hours - pH, oil & grease, NH3 - intake, feed to biox cells, final effluent from each clarifier, once-through cooling water.

* Crude unit and BTX have own cooling towers and so does hydrocracker - chlorine used to control algae growth; non-metallic corrosion inhibitor used.

B 1

REFINERY EFFLUENT MEASUREMENT, SAMPLING, ANALYSES, & TREATMENT

TEXACO, NANTICOKE

MEASUREMENT (flow)

INTAKE - measured but not used

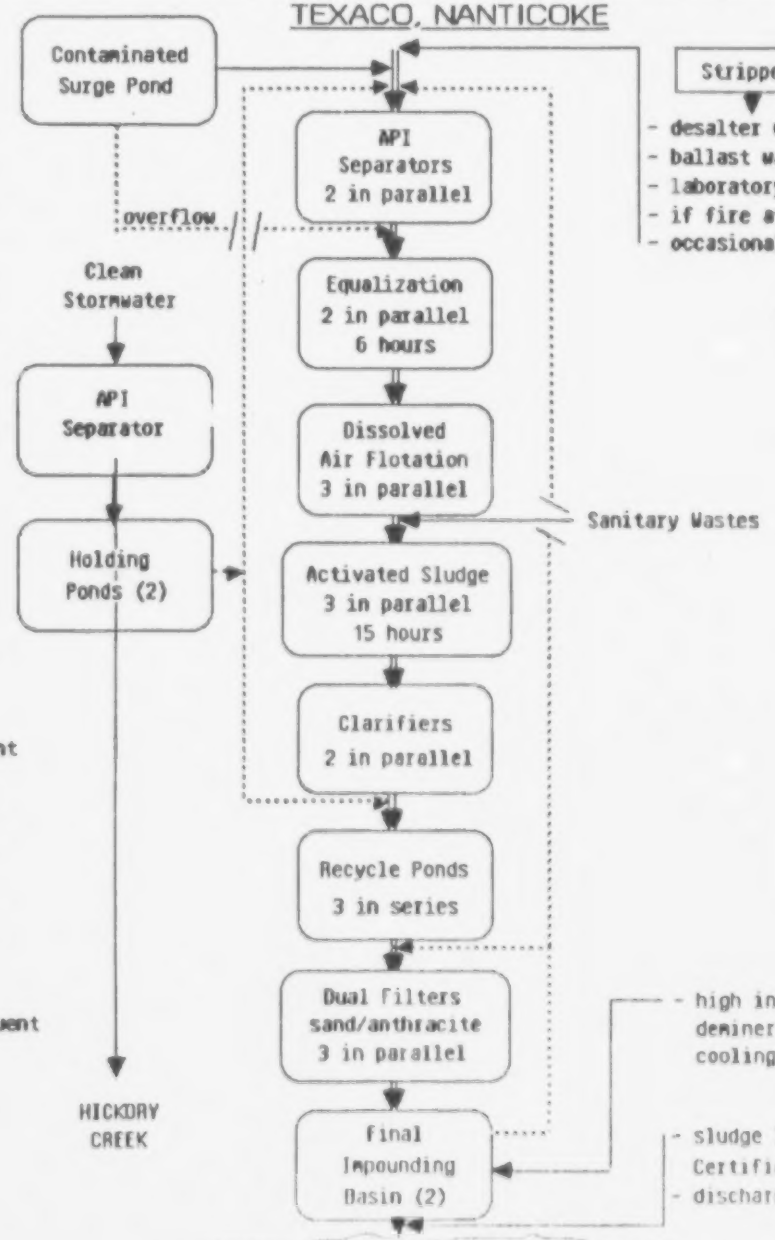
FINAL EFFLUENT - measured by orifice, recorded and integrated

Within treatment system
- flow from DAF measured and used in treatment system control
- clean stormwater flow measured, recorded & integrated and discharged

SAMPLING
- 24 hour composite/day, 7 days/week
- fixed volume sample

ANALYSES
- every day phenolics & pH since phenolics are good indicators of change in treatment
- 3 days/week - TSS, oil & grease, sulphide, NH4 & more frequently if required
- 96 hour static fish toxicity once/month but federal requirement only 24 hour results
- clean stormwater analyzed for 6 pollutants before discharged as a batch
- automated ammonia and phenolics analyses are used for treatment operation

SAMPLING POINTS
- used by operator to control effluent treatment
- before & after API Separator
- inlet to DAF
- inlet to activated sludge
- effluent from clarifier
- inlet & outlet dual filter
- final effluent



Stripper
- sour water
- tank bottoms water (periodic flow)

- desalter wastewaters (fresh caustic)
- ballast water
- laboratory wastewaters
- if fire at units, pad water
- occasional water from decoking furnace tubes

NOTE:
- effluent treatment system consists of two parallel trains of equipment; either train can handle entire normal refinery waste waters
- adjustment of pH at equalization basin is automatic, can add caustic or acid
- steam is injected automatically to maintain temperature at inlet to activated sludge cells
- capable of recycling from any final impounding basin to activated sludge cells or API Separater or dual filter
- capable of sending clean stormwater to API Separator or dual filter; test clean stormwater for 6 conventional pollutants before discharge

- high inorganic solids wastewaters from boiler water demineralization unit, blowdown from boilers and cooling tower
- sludge landfarm leachate (limits set by MOE Certificate of Approval)
- discharged on batch basis after analysis

APPENDIX C

DISCUSSION OF ANALYSIS METHODS

From PACE Summary Report (14)

ANALYTICAL METHODOLOGY

When the U.S. Environmental Protection Agency introduced legislation listing 129 specific contaminants, it became necessary for laboratories to research methodologies and enhance instrumentation capabilities. Most private and public sector laboratories in Canada and the U.S. were not equipped to carry out analyses for the full list.

After considerable research the EPA published the methodology for priority pollutant analysis in 1979 (2) and these methods were adopted for the PACE investigations.

The analytical methodology is presented in detail for each study as an appendix and summarized in the text of each of the reports. It should be stressed that the methods, being primarily based on multi-component analysis are not as precise and accurate as single component analysis. There is a trade-off made when a number of compounds must be analysed at one time. A large percentage of the analyses, undertaken in the PACE project, were designed to define the precision and accuracy of the analytical methodology and are further discussed in section 7.0.

The most important instrument required to perform the priority pollutant analysis, a gas chromatograph/mass spectrometer (or GC/MS). GC/MS was developed in the mid 1960's, well prior to the onset of contaminants legislation — in fact it was preliminary research and subsequent publications by scientists working with GC/MS that enhanced the public's awareness of the contaminants problem. All but fifteen of the pollutants on the EPA Priority Pollutant List are organic compounds. For this reason GC/MS instrumentation is ideally suited for their detection and quantitation in wastewaters.

In an analysis, individual compounds are separated by the gas chromatograph (GC) portion of the instrument. They then enter the mass spectrometer (MS) where a "finger-print", known as a mass spectrum is produced for each. This mass spectrum fingerprint is compared with those stored in a computerized data system and if a match is found the compound is identified. A more detailed description of GC/MS is presented in Appendix 2.

Analysis of Wastewater

Conventional Parameters and Metals: The conventional parameters are defined as those normally carried out on refinery wastewaters and include pH, suspended solids, sulfide, oil and grease, ammonia, and phenol. The analyses were carried out using well established procedures described in "Standard Methods" published by American Public Health Association APHA (11). As required by the Environment Canada regulations, methodologies outlined in the 13th edition of APHA (12) were used for analyses pertaining to oil and grease, ammonia, sulfide and total phenolics.

The metals were analysed by specific atomic absorption methods and by ICP (Inductively Coupled Plasma).

Volatile Compounds: This group is referred to as the "Purgeable Fraction" on the EPA Priority Pollutant list (see Table 1) and defined as those compounds that are less than two percent soluble in water, boil at or below 150 degrees C and are amenable to analysis by gas chromatography. Samples were analysed by a "purge and trap" system coupled to a GC/MS as described by EPA method 624 (2).

Acidic and Base-Neutral Compounds: These groups are referred to as the "Acid Fraction" plus "Base-Neutral Fraction" on the EPA Priority Pollutant list and defined as those compounds that are solvent extractable and amenable to analysis by gas chromatography. Samples were analysed by extracting a 1.5 litre volume first at pH 11 and then at pH 2. The solvent phase from each extraction was concentrated to produce the base-neutral and acid fractions respectively. These fractions were then analysed by GC/MS. This analysis is described by EPA method 625 (2).

In the first study, the seven refinery survey, the polynuclear aromatic hydrocarbons (PAH), which are part of the base-neutral fraction, were also quantified by a high pressure liquid chromatography (HPLC) in order to enhance sensitivity.

Pesticides and Related Halogenated Hydrocarbons: The halogenated pesticides and related compounds such as polychlorinated biphenyls (PCB), polybrominated biphenyls (PBB), etc. are also solvent extractable but are analysed as a separate group since a high degree of analytical sensitivity is required. The analyses were carried out using a hexane extraction followed by clean-up and then analysed by gas chromatography (GC) with electron capture (EC) detection, which is more sensitive than GC/MS methods.

Analytical Quality Assurance

In the seven refinery study, a rigorous quality control/quality assurance program was used to evaluate the methodology. The effectiveness of measures taken to avoid field and laboratory contamination was evaluated by analysing a series of transportation blanks. The adequacy of the methods used for the isolation and analysis of the parameters under investigation was evaluated by analysing seven effluents "spiked" with a mixture of compounds representing most of the parameters on the study list.

In the later studies, a new approach for assessing analytical methodology was used based on the use of deuterated compounds which became generally available in the early 1980's. Deuterated compounds have different molecular weights than the corresponding authentic compounds and can therefore be quantified separately. In this manner, quality control (i.e. spike and recovery) data can be generated for each sample analysed. For the later PACE studies almost every sample analysed was "spiked" with a number of deuterated priority pollutants as a check on analytical precision and accuracy.

Brief Description of GC/MS

In the 1950's and 1960's organic chemical analysis was carried out using a gas chromatograph (GC). The function of a GC is as follows:

- separate a mixture of compounds into individual components (usually relies on the compounds physical and chemical nature (volatility, polarity,, molecule size, etc.)
- detect and quantify each individual compound as it is eluted (the detector response is proportional to the concentration).

Under certain conditions the elution (retention) time and detector response (peak height/area) can be determined for any one compound. This allows one to determine the composition of an unknown by comparing the retention times and peak size with those of a known standard. The major drawback of this type of analysis is that sample peaks that do not match the retention times for the calibration standards are not often identified. Therefore the instrument is usually only used when the analyst is looking for a target list of compounds. Even when the peaks do match the standards, the identity of the compound is not necessarily confirmed.

In the mid 1960's scientists developed ways of interfacing a mass spectrometer (MS) to a gas chromotograph. Thus, the MS became, in essence, a very specialized and highly sophisticated detector for the GC. With these two instruments coupled together, the individual compounds separated by the GC enter the MS and a "finger-print" known as a mass spectrum is produced for each. This mass spectrum is compared with all those stored in a computer library associated with the instrument and if a match is found the compound is identified. A schematic showing GC/MS instrumentation is shown in Figure 1.

In the period between 1975-1980, GC/MS instrumentation advanced significantly especially with regard to computer search capabilities and libraries. The newer instruments were programmed to allow rapid identification of an unknown compound by comparing its mass spectrum with over 30,000 organic compounds in a reference library.

When a wastewater sample is analysed by GC/MS it is not uncommon to detect numerous, perhaps hundreds of individual compounds. When samples are routinely analysed for EPA Priority Pollutants, an analyst will not normally attempt to identify all the compounds detected. Rather, the standard approach is to search for a "target" list of compounds and confirm the presence or absence of these substances.

To accomplish this, the GC/MS instrument is programmed to identify only those target compounds and by analysing standards containing known concentrations of these compounds, quantitation is also accomplished. The data is stored in the computer so it is possible to identify the other substances if required. For the PACE studies, the samples were analysed:

quantitatively — for specific target lists of compounds, and,
qualitatively — to identify other compounds that may be present.

By approaching the project in this manner, it was possible to make definite statements concerning the types of compounds that *were* and *were not* routinely detected in refinery wastewaters. Also quantitative information was established for a predetermined list of compounds.

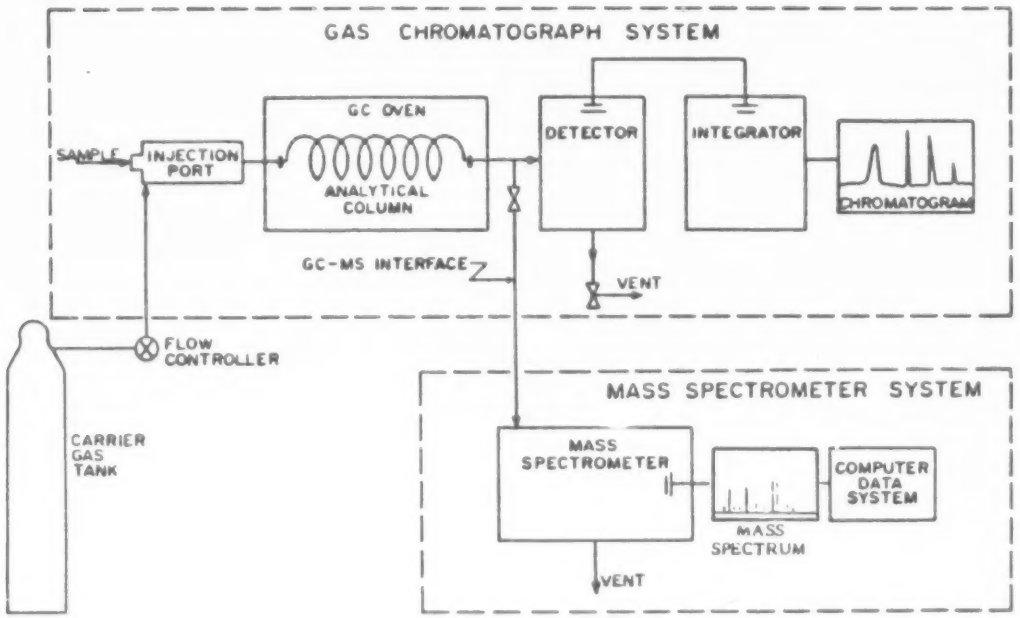


Figure 1. Schematic drawing of a gas chromatograph — mass spectrometer (GC/MS) showing the individual components as discussed